

---

*MONOGRAPHS ON INDUSTRIAL CHEMISTRY*  
*EDITED BY SIR EDWARD THORPE, C.B., LL.D., F.R.S.*

PLANTATION RUBBER  
AND THE  
TESTING OF RUBBER

---

# PLANTATION RUBBER AND THE TESTING OF RUBBER

BY  
G. STAFFORD WHITBY

PH.D., M.Sc., A.R.C.Sc.

ASSISTANT PROFESSOR, DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY

*WITH PLATES AND DIAGRAMS*

LONGMANS, GREEN AND CO.

39 PATERNOSTER ROW, LONDON

FOURTH AVENUE & 30TH STREET, NEW YORK

BOMBAY, CALCUTTA, AND MADRAS

1920



## INTRODUCTION

WITHIN the present decade the rubber industry has undergone great expansion. The chief impulse to this expansion came from the development of the automobile. This development produced a demand for rubber for the purpose of manufacturing tyres, which the supply of wild rubber was unable to meet, and which led to a vast expansion in the already-established plantation industry of the Eastern tropics. During the years 1909-10 the price of raw rubber rose to an unprecedentedly high level; and there followed a spectacular "boom" in rubber planting and a less spectacular boom in the manufacture of rubber goods, particularly of tyres.

The extent to which the rubber industry has expanded during the present decade may be gathered from the fact that the world's production of raw rubber in 1917 (the last normal year) was 3.64 times as large as in 1910. This increased production is entirely accounted for by an increase in the production of plantation rubber, which grew in amount from a quantity forming in 1910 11.6 to a quantity forming in 1917 79.5 per cent. of the total production. The increased production of raw rubber has been absorbed chiefly by the rubber manufacturing industry in the United States, which consumed 5.76 times as much raw rubber in 1917 as in 1910.

The following table shows the salient statistics regarding the volume of raw rubber production from a time when plantation rubber began to be produced in noticeable quantities.

The above statistics are represented graphically in Fig. 1, at the back of the volume.

It will be observed that during the period of great expansion in plantation rubber production, the production of rubber from wild trees in the region of the Amazon (Brazilian rubber) has maintained its volume, but that the production of wild

TABLE I<sup>1</sup>

Year	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917
A. World's production (tons)	66,210	60,000	65,400	60,600	70,500	75,149	98,928	108,440	120,380	158,702	201,598	256,976
Increase on preceding year (per cent.)	6.5	4.2	—5.2	6.4	1.2	6.5	31.6	9.6	11.0	31.8	27.0	27.4
B. Plantation production	510	1,000	1,800	3,600	8,200	14,419	28,518	47,618	71,380	107,867	132,650	204,348
Percentage of A	0.7	1.4	2.8	5.2	11.6	19.2	28.8	43.9	59.3	67.9	75.7	79.5
C. Brazilian production	36,000	38,000	39,000	42,000	40,800	37,730	42,410	30,370	37,000	37,220	36,500	39,370
D. Production of other wild rubber	29,700	30,000	24,600	24,000	21,500	23,000	28,000	21,452	12,000	13,615	12,448	13,258
E. Consumed in the U.S.	28,483	28,634	28,950	30,669	31,576	29,235	50,248	49,851	61,251	96,792	116,475	175,000
F. " Great Britain	13,838	15,913	10,828	15,107	20,455	16,736	18,724	25,276	18,549	15,072	26,760	25,953
G. Plantation acreage in bearing	—	—	—	—	93,205	237,240	402,912	545,385	681,355	885,079	1,200,407	1,448,933
Average yield per acre	—	—	—	—	107	136	158	195	234	273	284	316
H. Average price of plantation rubber	5.10½	4.11½	4.2½	7.1	8.9	5.5½	4.9	3.0½	2.3½	2.6	2.10½	3.1½
I. " " fine hard Para	5.2½	4.6	4.10½	6.11	8.10	5.0	4.10	3.8	2.10½	2.7	3.1½	3.1½

<sup>1</sup> Messrs. W. H. Rickinson & Son's data. 1918, on account of war restrictions, was not a normal year as regards the production of rubber. The estimated figures for 1918 are as follows: World's production, 241,579; plantation, 200,950; Brazilian, 39,700; rest, 9929. The estimated figures for 1919 are as follows: World's production, 339,000; including 35,000 from 1918; plantation, 339,000; Brazilian, 35,000; rest, 3532 (*The World's Rubber Position*, August 1919, W. H. Rickinson, 3 Great Winchester Street, London, E.C.).

rubber from other sources (chiefly African) has declined very considerably.

The total area now under plantation rubber is nearly 2,000,000 acres. Almost half of this area is situated in the Malay Peninsula. Next to the Malay Peninsula in the magnitude of its planted rubber area is Sumatra, on the other side of the Straits of Malacca. Both these countries, lying close to the equator, possess a climate particularly suitable for the growth of rubber: the climatic conditions are remarkably uniform throughout the year; the temperature, which is sufficiently high (although not so high as the temperatures which may be recorded at times on a large land mass such as India), shows only slight fluctuations throughout the year; the prevailing humidity is high; the rainfall is high and is very evenly distributed throughout the year.<sup>1</sup> Next to Sumatra in magnitude of area come Ceylon and Java, situated a little further, north and south respectively, from the equator, and possessing climates not quite so favourable to the growth of rubber as the climate of the Malay Peninsula and Sumatra. Smaller areas of rubber have been planted in Southern India, Borneo, Burmah, Cochin China and Fiji.

The tree cultivated on rubber plantations has been almost exclusively *Hevea brasiliensis*. A number of other species, particularly *Manihot glaziovii*<sup>2</sup> (the source of Ceara rubber<sup>3</sup>) and *Funtumia elastica*<sup>4</sup> in Africa, *Castilloa elastica*<sup>5</sup> (a source of "Caucho" rubber) in Mexico, and *Ficus elastica* (the source of Rambong or Assam rubber) in the Eastern tropics, have been used for the establishment of plantations; but, for a variety of reasons, including predominantly their lower yield of rubber as compared with the yield of *Hevea brasiliensis*, plantations of them have in general had little success; and, where the climatic and labour conditions are suited to the cultivation of *Hevea brasiliensis*,

<sup>1</sup> For a large amount of data relative to the climate of rubber-growing countries, see Herbert Wright, *Hevea brasiliensis*, 4th edition, London, 1912, p. 542. See also, e.g., van Bemmelen, "On the Climate of the Principal Rubber-producing Countries," *Rubber Recueil*, 1914, p. 145; Ulée, *Archief*, 1917, 1, 60; Meteorological data published regularly in the *Agric. Bull. F.M.S.* For data on the degree of humidity in Selangor, F.M.S.: Whitby, *J. Soc. Chem. Ind.*, 1918, 37, 278 T.

<sup>2</sup> See particularly A. Zimmermann, *Der Manihot, seine Kultur, Gewinnung und Präparation*, Jena, 1913, p. 342.

<sup>3</sup> The term Manicoba rubber has been used to distinguish Ceara rubber obtained from certain species of *Manihot*.

<sup>4</sup> Otherwise known as *Kickxia africana*. See particularly C. Christy, *The African Rubber Industry and Funtumia elastica*, London, 1911.

<sup>5</sup> See, e.g., P. Olsson-Seffer, *Lects. on Rubber*, 1908, p. 86; Ludewig, *Tropenpflanzer*, 1910, 14, 510.

have often given way to the latter.<sup>1</sup> The total quantity of rubber produced by plantations of species other than *Hevea brasiliensis* is so insignificant when compared with the quality of plantation *Hevea* rubber produced that for most purposes and throughout the present volume the term Plantation Rubber may, in the absence of qualification, be understood as Plantation *Hevea* Rubber.

The best-esteemed wild rubber being that obtained from *Hevea brasiliensis* (growing in the Amazon region), when, in the 'seventies, it was decided if possible to establish rubber plantations in the Eastern tropics, it was particularly to this species that attention was directed. A large number of seeds were secured in Brazil in 1876 by H. A. Wickham and were taken to Kew. From Kew, plants were sent to the Department of Agriculture in Ceylon.<sup>2</sup> Later, seeds were distributed from Ceylon throughout the Eastern tropics.<sup>3</sup>

During this recent period of expansion in the rubber industry

<sup>1</sup> Some years ago the author saw areas of *Ficus elastica* in Sumatra and in Java being cut down for the purpose of re-planting with *Hevea brasiliensis*. In another case with which he is acquainted, a company operating in the French Congo and possessing a plantation of 400,000 *Funtumia elastica* trees decided to make no further plantings of the latter species, but, instead, to direct attention to *Hevea brasiliensis*.

<sup>2</sup> It appears probable that a few of the trees from which the Eastern plantations originated were derived, through the agency of Kew, from seeds obtained by the collectors Collins (1873) and Cross (1877).

<sup>3</sup> For a history of the introduction of *Hevea brasiliensis* into Ceylon, see Petch, *Annals Roy. Bot. Gdns., Peradenyia*, 1915, Vol. V., No. vii. Also see Lock, *Rubber and Rubber Planting*, Cambridge, 1913, p. 6, *et seq.* There has been some discussion as to whether the seeds from which the plantations have been derived were obtained from the best variety of rubber tree in Amazonia. Cramer, who visited Brazil, believes (*Rubber Recueil*, 1914, p. 13) that the seeds were obtained from a district (Tapajoz) which yields, he asserts, rubber somewhat inferior to the best Brazilian rubber (from the Acre district); and he appears to be supported in this belief by Brazilian authorities (particularly Huber), who regard the Acre rubber as a distinct variety. The assertions which have been made in the course of this discussion as to the quality of rubber from particular districts on the Amazon are, however, unsupported by any exact or sufficient evidence. Doubtless, as Cramer contends (*Rep. Batavia*, 1914, p. 27), new strains of seeds from selected trees on the Amazon could with advantage be introduced to the East, just as seed selection on the plantations themselves would be advantageous. It is not impossible even that a new and better variety of *Hevea brasiliensis* could be introduced from Brazil. But it would appear, at all events, that, so far as the available data enable a comparison to be made between rubber produced in Brazil and rubber produced in the East, an average area of plantation *Hevea* is capable of yielding rubber as good as the average samples of rubber produced on the Amazon. Whitby found that two samples of rubber prepared in the Brazilian style from areas of plantation trees selected at random gave vulcanization results fully equal to those given by typical samples of rubber prepared in Brazil.

the intensive scientific study of rubber has begun, and, as will appear in the present volume, has already produced a not inconsiderable amount of valuable knowledge. The larger part of the most recent study, in so far as it has received publication, relates to the preparation of the raw rubber on the plantation.

The circumstance that the supply of raw rubber is now chiefly derived from plantations, where its preparation can be carried out under technical control, instead of, as formerly, being entirely derived from almost inaccessible forests, where no control was exercised over its preparation,<sup>1</sup> most certainly opens up new possibilities for the rubber industry as a whole. Their realization in full depends upon the development of coöperation between the producing end and the manufacturing end of the industry.

The recent study of exact methods of testing rubber bears an essential relation to the study of the preparation of plantation rubber, and, in the aspects considered in the chapters on the Evaluation of Raw Rubber in Part II of the present volume, has been developed largely by workers connected with the plantation industry.

In Part II of this volume is also given an account of investigations made by physicists into the physical properties of rubber. These investigations, although for a large part comparatively remote in date and without immediate practical bearing, have been described in considerable detail, because of their frequent suggestiveness, and of the circumstance that hitherto they have been almost entirely overlooked by rubber technologists. The (generally excusable) failure in these investigations to appreciate how wide is the variety of mixtures which may be described as "rubber," and how greatly the physical properties of "rubber" are susceptible of variation as a result of variation in the character of the mixtures used and in the conditions of vulcanization (most of the investigators describe their material merely as "rubber"), detracts a little from the direct value of these investigations, but hardly from their suggestiveness. It would seem desirable that some at least of the studies which have been made by physicists on the properties of rubber should be extended over a wider range of physical effects, and with reference to systematic variations in the character of the rubber

<sup>1</sup> The fact is not overlooked that possibly the circumstance that wild rubber is prepared by natives on traditional lines may confer upon some sorts a greater uniformity than marks the plantation sort. But any advantage that wild rubber possess on this account need not be and is not likely to be permanent.

"compounds" and in the conditions of vulcanization. It would not be unfair to say that, in proportion to the importance of rubber as a constructional material in modern life, and considering the uniqueness of its properties, the physical properties of rubber have not yet received their due amount of exact experimental study.

The author wishes to express his thanks to the following for permission to reproduce diagrams illustrative of their work; namely : Prof. A. S. Barnes, Prof. H. Bouasse, Mr. B. J. Eaton, Dr. K. Gottlob, Mr. F. C. van Heurn, Dr. K. Memmler, Dr. P. Schidrowitz, Mr. L. Schopper, Dr. H. P. Stevens, and Dr. O. de Vries. He also wishes to thank Mr. H. Ernst, Sumatra, for permission to reproduce photographs taken by him, and forming Plates I, IV, V and VI.

# CONTENTS

CHAP.	PAGE
INTRODUCTION . . . . .	v
LIST OF ILLUSTRATIONS . . . . .	xiii
ABBREVIATIONS . . . . .	xv

## PART I

### THE PREPARATION OF PLANTATION RUBBER

I. THE RUBBER TREE AND THE EXTRACTION OF LATEX	3
II. LATEX AND ITS COAGULATION . . . . .	31
III. THE RESIN . . . . .	76
IV. THE PROTEIN . . . . .	108
V. COLLECTION OF LATEX—COAGULATION IN THE FACTORY . . . . .	124
VI. CRÊPE . . . . .	151
VII. SHEET . . . . .	168
VIII. MATURATION . . . . .	186
IX. VARIATION . . . . .	201

## PART II

### THE TESTING OF RUBBER

X. THE STRESS-STRAIN RELATIONS OF RUBBER—THE MODULUS OF ELASTICITY . . . . .	219
XI. TECHNIQUE OF TENSILE TESTS . . . . .	259
XII. TECHNIQUE OF VULCANIZATION TESTING . . . . .	281
XIII. PROGRESSIVE CHANGES ON VULCANIZATION . . . . .	302
XIV. COMPARISON OF RAW RUBBER SAMPLES . . . . .	340
XV. STABILITY OF STATE OF CURE . . . . .	367

## CONTENTS

CHAP.		PAGE
XVI.	TECHNICAL MIXES . . . . .	387
XVII.	VISCOSITY DETERMINATIONS . . . . .	402
XVIII.	CYCLES OF EXTENSION AND RETRACTION—HY- STERESIS . . . . .	410
XIX.	ELASTIC AFTER-EFFECT . . . . .	424
XX.	RELATION OF THE THERMAL, OPTICAL AND ELEC- TRICAL TO THE MECHANICAL BEHAVIOUR OF RUBBER . . . . .	453
XXI.	POISSON'S RATIO . . . . .	486
	BIBLIOGRAPHY . . . . .	503
	INDEX . . . . .	549



## LIST OF ILLUSTRATIONS

PLATE	PLATES	Facing page
I.	Young Trees in First Year of Tapping . . . . . <i>(From photograph by H. Ernst, Sumatra)</i>	12
II.	Trees tapped by "V" Cuts . . . . .	16
III.	Older Tree tapped on Renewed Bark . . . . .	16
IV.	Interior of Milling Shed . . . . . <i>(From photograph by H. Ernst, Sumatra)</i>	156
V.	Crêpe Drying Shed . . . . . <i>(From photograph by H. Ernst, Sumatra)</i>	162
VI.	Sorting and Packing Latex Crêpe . . . . . <i>(From photograph by H. Ernst, Sumatra)</i>	214
VII.	Schopper Tensile Testing Machine . . . . .	268
VIII.	Schopper's Ring Punching Machine and "Automatic" Micrometer . . . . .	299

FIG.		PAGE
I.	World's Rubber Production. (Chart) . . . . . <i>At end of Vol.</i>	
2.	Tree-yield Frequency Curve . . . . .	6
3.	Influence of Resin on Stress-Strain Curves . . . . .	90
3a.	Stress-Strain Curves of Sheets Matured for Various Periods	193
4.	Diagram . . . . .	220
5.	Typical Stress-Strain Curve for High-grade Rubber . . . . .	222
6.	Diagram . . . . .	229
7.	Apparatus for Dynamical Method of Measuring Elastic Modulus . . . . .	231
8.	Relation between $\epsilon$ and $\Delta$ . . . . .	233
9.	Apparatus for Statical Method of Measuring Elastic Modulus . . . . .	235
10.	Relation between $\epsilon$ and $\Delta$ . . . . .	238
11.	Variation of Modulus Determined by the Method of Stationary Waves . . . . .	243
12.	Stress-Strain Curve on Compression . . . . .	249
13.	Hysteresis Loops on Compression . . . . .	252
14.	Diagram . . . . .	257
15.	Diagram of Simple Wedge Grips . . . . .	262
16.	Dumb-bell-shaped Test Piece . . . . .	263
17.	Variation in Stress from the Outside to the Inside of a Ring . . . . .	264
18.	Stress-Strain Curves for Six Rubbers . . . . .	269

FIG.		PAGE
19.	Stress-Strain Curves for Longitudinal, Transverse and Ring Test-Pieces . . . . .	271
20.	Breaking-Points of Rings of Different Cross Sections . . . . .	274
21.	Influence of Temperature on Breaking Figures and on Set . . . . .	280
22.	Stress-Strain Diagrams for Samples of Raw Rubber . . . . .	284
23.	Change of Breaking Figures and Combined Sulphur with Prolongation of Vulcanization Time . . . . .	316
24.	Stress-Strain Curves of Slab, Sheet and Crêpe at Different Cures . . . . .	318
25.	Stress-Strain Curves and Average Breaking-Points for a Sample Cured for Different Periods of Time . . . . .	320
26.	Stress-Strain Curves for Slab, Sheet and Crêpe Cured for Various Periods of Time . . . . .	322
27.	Curves for the Same Sample Cured with Different Proportions of Sulphur . . . . .	326
28.	Breaking-Points of Five Samples of Rubber . . . . .	328
29.	Change of $P_B$ on Progressive Curing with Different Proportions of Sulphur . . . . .	329
30.	Breaking-Points of Rubber-Sulphur Mixes Containing 7.5, 6 and 5 per cent. of Sulphur . . . . .	331
31.	Breaking-Points of Fast- and Slow-Curing Rubbers with Different Proportions of Sulphur . . . . .	335
32.	Curves . . . . .	345
33.	Relation between Vulcanization Co-efficient and Position of Stress-Strain Curve . . . . .	364
34.	Change of Tensile Strength on Accelerated Ageing . . . . .	370
35.	Movement of Stress-Strain Curves during Accelerated Ageing . . . . .	377
36.	Movement of Stress-Strain Curve on Continued Curing with 10 and with 4.8 per cent. Sulphur . . . . .	384
37.	Mixes containing (a) Inorganic Ingredients, (b) Different Proportions of Sulphur (Stress-Strain Curves) . . . . .	400
38.	Viscosity and Tensile Strength of a Number of Estate Samples . . . . .	406
39.	Viscosity and Time of Cure of a Number of Estate Samples . . . . .	407
40.	Cycles of Extension and Retraction . . . . .	412
41.	Cycles of Ascending and Descending Amplitude . . . . .	414
42.	Cycles at Different Rates . . . . .	415
43.	Cycles at Different Temperatures . . . . .	417
44.	The Schwartz Hysteresis Machine . . . . .	418
45.	Hysteresis Loops for Different Types of Rubber . . . . .	422
46.	After-Strain under Different Loads . . . . .	439
47.	Relation between Set and "Slope" for a Number of Samples . . . . .	450
48.	Diagram . . . . .	491

## ABBREVIATIONS

<i>Agric. Bull. F.M.S.</i>	. The Agricultural Bulletin of the Federated Malay States.
<i>Annalen</i>	. . . . . Liebig's Annalen der Chemie.
<i>Ann. der Phys.</i>	. . . . . Annalen der Physik (Poggendorff's Annalen, Wiedemann's Annalen, Drude's Annalen).
<i>Archief</i>	. . . . . Archief voor de Rubbercultuur in Nederlandsch-Indië.
<i>Beibl. Phys.</i>	. . . . . Beiblätter zu den Annalen der Physik.
<i>Ber.</i>	. . . . . Berichte der Deutschen Chemischen Gesellschaft.
<i>Chem. Met. Eng.</i>	. . . . . Chemical and Metallurgical Engineering.
<i>Cimento</i>	. . . . . Il nuovo Cimento, Giornale di Fisica, di Chimica e Scienze Affini.
<i>C.R.</i>	. . . . . Comptes rendus de l'Académie des Sciences.
<i>Delft Communics.</i>	. . . . . Communications of the Netherland Government Institute for advising the Rubber Trade and the Rubber Industry established at Delft.
<i>Dept. Agric. Ceylon, Bull.</i>	. Department of Agriculture, Ceylon, Bulletin.
<i>Dept. Agric. F.M.S., Bull.</i>	. Department of Agriculture, F.M.S., Bulletin.
<i>Fortschr. Phys.</i>	. . . . . Die Fortschritte der Physik.
<i>Gummi-Ztg.</i>	. . . . . Gummi-Zeitung (Berlin).
<i>I.R.J.</i>	. . . . . The India-Rubber Journal (London).
<i>I.R.W.</i>	. . . . . India-Rubber World (New York).
<i>J. Amer. Chem. Soc.</i>	. . . . . Journal of the American Chemical Society.
<i>J. Ind. Eng. Chem.</i>	. . . . . Journal of Industrial and Engineering Chemistry.
<i>J. Soc. Chem. Ind.</i>	. . . . . Journal of the Society of Chemical Industry.
<i>Koll. Zeit.</i>	. . . . . Kolloid Zeitschrift (Zeitschrift für Chemie und Industrie der Kolloide).
<i>LB</i>	. . . . . Percentage length at break.
<i>Le Caoutchouc</i>	. . . . . Le Caoutchouc et la Gutta-Percha (Paris).
<i>Lects. on Rubber</i>	. . . . . Lectures on India Rubber. The official account of the Conference held in connection with the International Rubber and Allied Trades Exhibition, London, 1908. Edited by D. Spence.
<i>Meded. Delft</i>	. . . . . Mededeelingen van den Rijksvoorlichtingsdienst ten behoeve van den Rubberhandel en de Rubbernijverheid te Delft.
<i>Meded. over Rubber</i>	. . . . . Mededeelingen over Rubber, Department van Landbouw, Nijverheid en Handel in Nederlandsch-Indië.

<i>Mitt. Prüfungsamt</i>	. . .	Mitteilungen aus dem Königlichen Materialprüfungsamt.
PB <sup>1</sup>	. . . . .	Breaking stress (unless otherwise stated, in kg. per sq. mm. of original cross-section).
<i>Rec. trav. chim.</i>	. . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rep. Batavia</i>	. . .	Report of the International Rubber Congress and Exhibition, Batavia, 1914 (Weltervreden, 1915).
<i>Repertorium</i>	. . .	Repertorium der Physik (Repertorium für Experimental-Physik, Carl's Repertorium, Exner's Repertorium).
<i>Rubber Industry</i>	. . .	The Rubber Industry. Official Reports of the Third (1911) and of the Fourth (1914) International Rubber Congresses, London.
<i>Rubber Recueil</i>	. . .	Rubber Recueil. International Rubber Congress and Exhibition, Batavia, 1914 (Amsterdam, 1914).
<i>Sitzungsber. Wien</i>	. . .	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
<i>Trans. Chem. Soc.</i>	. . .	Transactions of the Chemical Society.

---

<sup>1</sup> Factor for converting kg./mm.<sup>2</sup> to lb./in.<sup>2</sup> = 1422.4. Factor for converting lb./in.<sup>2</sup> to kg./mm.<sup>2</sup> = 0.000703.

PART I  
THE PREPARATION OF PLANTATION RUBBER

## CHAPTER I

### THE RUBBER TREE AND THE EXTRACTION OF LATEX

A CONSIDERABLE amount of the rubber in Ceylon is inter-planted with tea, and a small amount of that in Java and Sumatra is inter-planted with coffee; but for the most part rubber alone is grown on the plantations. Also: a certain amount of rubber has been planted on land originally cleared for other crops; but for the most part newly-cleared, virgin-jungle land has been used. The planting has been done with seed, sometimes planted out directly at stake, sometimes planted out as seedlings, but perhaps most usually planted out as stumps, after growing for several months in nurseries.

*The seeds and seed oil.*—It may be mentioned here, as a point of secondary interest, that *Hevea brasiliensis* yields a large crop of seed which has been found to contain a high proportion of an oil, inferior in drying properties to linseed oil, but probably capable of replacing the latter for a number of purposes. It appears likely that the oil will prove to be of industrial value. The present writer found the following data for fresh seed: 1000 seeds weigh 10 lb.; *ca.* 850 seeds occupy 1 gallon; the fresh kernels form on the average 62.5 per cent. of the weight of the seeds and contain 31 per cent. of water; the dry kernels forming 43 per cent. of the weight of the seed. Spring and Day<sup>1</sup> report the weight of air-dried seeds as 8 lb. 6 oz. per 1000. They estimate the average annual yield of seed per tree as 400 seeds, equivalent, at 90 trees per acre, to 306 lb. of seed per acre. They find that the seeds keep well if sun-dried; and that they yield on extraction about 27 per cent. of oil. Referred to the sun-dried kernels, the oil yield on extraction was 47.5 per cent. Nitrogen in the dried kernels was equivalent to 15.3 per cent. protein. An examination of the oil and cake made at the Imperial Institute showed the following results<sup>2</sup>:—

Extracted oil.—Sp. gr. 15°, 0.925–0.930; acid value, 10.7–40.9; saponification value, 188.5–192.1; iodine value (per cent.), 128.3–

<sup>1</sup> *Agric. Bull. F.M.S.*, 1918, 6, 231.

<sup>2</sup> *Bull. Imp. Inst.*, 1913, 9, 551. Cf. also *Agric. Bull. F.M.S.*, 1919, 7, 73. For analyses of earlier samples, vide *Bull. Imp. Inst.*, 1903, 1, 156.

143.3. The cake gave analytical results very similar to the results given by linseed cake. Feeding trials showed the cake to be a very satisfactory cattle food.

It was observed by van Romburgh<sup>1</sup> that seeds of *Hevea brasiliensis* gave acetone and hydrocyanic acid on distillation. Gorter<sup>2</sup> has, more recently, isolated from the seeds the cyanogenetic glucoside the hydrolysis of which was responsible for the production of these substances, and has found it to be identical with the glucoside, phaseolunatine, originally isolated by Dunstan and Henry<sup>3</sup> from the bean, *Phaseolus lunatus*. He found the fresh, husked seeds to yield 0.077 per cent. of hydrocyanic acid, equivalent to 0.7 per cent. of phaseolunatine. By extracting 475 g. of husked seed with boiling alcohol, treating the extract with calcium carbonate and lead acetate, and evaporating to crystallizing point, he obtained 2 g. of material, which, after re-crystallization from alcohol, agreed in melting point, optical activity, proximate analysis, and in yielding hydrocyanic acid, acetone and glucose on hydrolysis, with phaseolunatine.

#### SEED SELECTION. VARIATION

*Data on variation in yield.*—Extension of the area under plantation rubber went on so rapidly, that, despite the recognition, in a qualitative way, of very considerable differences in the yielding capacity of individual trees, and despite the examples afforded by temperate cultures, such as sugar-beet, and by tropical cultures, such as cinchona and sugar-cane, of the possibilities, in regard to yield improvement and resistance to disease,<sup>4</sup> which lay in seed selection, rubber seed selection received little or no attention, and was, perhaps, under the conditions, hardly feasible. With the exception of a few small experimental areas, the Eastern plantations have been grown entirely from non-selected seed. Some quantitative data on the extent of variation of rubber-yield in *Hevea brasiliensis* are now becoming avail-

<sup>1</sup> *Ann. du Jardin Bot. de Buitenzorg*, 1899, Vol. XVI.

<sup>2</sup> *Rec. trav. Chim.*, 1912, 31, 264.

<sup>3</sup> *Proc. Roy. Soc.*, 1904, 72, 285.

<sup>4</sup> It may be remarked here that plantation conditions, particularly in Malaya and Sumatra (where vast and almost uninterrupted areas are planted with this single species, where the humidity is always high, and where many stumps and logs, left from the recently-cleared jungle, occur over the planted areas), are exceptionally favourable to the spread of fungus diseases. The potential menace involved in this circumstance is, it is satisfactory to note, being increasingly recognized by those directing the plantations. For an authoritative statement with reference to it, see Sharples, "The Significance of Disease in the Economy of Malayan Rubber Plantations," *Kew Bull.*, 1917, No. 6; *I. R. J.*, 1917, p. 687.

able. The extent of variation is found to be very considerable and to suggest great possibilities for the selection of seeds or clippings. Such possibilities are more especially of interest with regard to areas which are to be planted in the future, but they are also of interest with regard to improving the yield of already-planted areas by means of selective thinning-out.

Observations were first made on the extent of variation in rubber yield among individual trees of *Hevea brasiliensis* by Whitby.<sup>1</sup> It was concluded that trees presented characteristic differences in their rubber-yielding capacity. Although the exact magnitude of the yield of rubber given by a tree on any one occasion was affected by variations in fortuitous circumstances, particularly by the rainfall and the season, yet the order of the magnitude was approximately constant for a given tree. Rutgers<sup>2</sup> has come to the same conclusion. He compared the classification, from the point of view of rubber-yield, of three large groups of trees after the lapse of periods of ten to twenty months with the original classification; and, as a result, concluded that "good trees remain good, poor trees poor."<sup>3</sup> Whitby determined the variation of rubber-yield from the individual trees in a population of 1011 seven-year-old trees on an apparently-uniform and typical area, planted 20 × 20 ft., in the Malay States. The yield<sup>4</sup> recorded for each tree was the mean of the

<sup>1</sup> For a preliminary notice, see *Plantation Problems of the Next Decade*, Weltervreden, 1914. For complete data, *Ann. Bot.*, 1919, **31**, 313.

<sup>2</sup> *Archief*, 1919, **3**, 105.

<sup>3</sup> Cf., for data incidentally supporting this conclusion, the records for the original generation of trees raised from the seeds first introduced into the East from Brazil, *Dept. Agric. Ceylon, Bull.*, Nos. 4, 13. Tapping records during 1908-13 for a famous tree planted at Heneratgoda, Ceylon, in 1877, show this tree as giving a high yield with noteworthy consistency. During each month of the three years 1911-13 this tree gave approximately 225 g. of rubber per tapping with marked regularity.

<sup>4</sup> The yields were determined by coagulating the latex, crèping the coagulum, and weighing the crèpe when it was dry. It should be pointed out that it would appear to be impermissible to classify trees according to yield by the simpler procedure of measuring the volumes of latex. For the rubber-content of the latex from trees of the same age, in the same situation and under the same tapping conditions, was found to vary considerably (Whitby, *loc. cit.*, 314). In the case of 245 trees forming a part of the population here in question, the rubber-content of the latex varied in the manner shown by the following frequency table.

TABLE II

VARIATION IN RUBBER-CONTENT OF LATEX FROM 245 INDIVIDUAL TREES

Gm. rubber per 100 cc.	23	24-25	26-27	28-29	30-31	32-33	34-35	36-37	38-39	40-41	42-43	44-45	46-47	48-49	50-51	52-53	54-55
Frequency	4	2	7	11	16	27	44	35	23	32	17	12	5	1	4	3	2
Mean = 36.58	0.25 per cent. $\sigma = 5.86 \pm 0.17$ per cent. $CV. = 16.02 \pm 0.49$ per cent.																

Mean = 36.58 0.25 per cent.  $\sigma$  = 5.86  $\pm$  0.17 per cent. CV. = 16.02  $\pm$  0.49 per cent.



yields determined on six to twelve separate days distributed over a typical period of the year. The trees were in their third year of tapping. In the two years previous they had been tapped by "basal" V cuts; and at the time of the observations were being tapped with a V cut on the next higher section of the trunk; the tapping cut being at the beginning of the period of observations 28-30 in. from the ground. The following frequency table shows the extent of the variation of rubber-yield found in this population:—

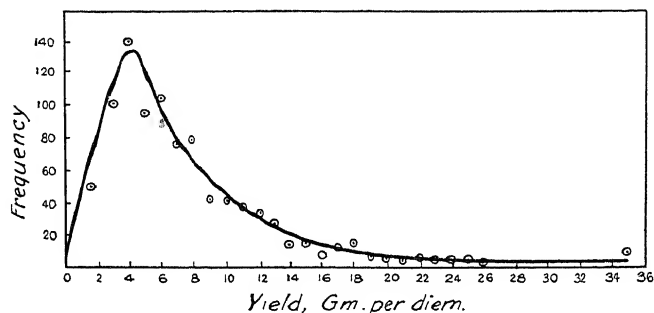
TABLE III

RUBBER YIELD FROM POPULATION OF 1011 SEVEN-YEAR-OLD *HEVEA BRASILIENSIS*

Grm. per diem	0-1.5	2	3	4	5	6	7	8	9	10	11	12	13	14
Frequency	55	84	101	140	95	104	76	78	42	41	37	34	26	13
Grm. per diem	15	16	17	18	19	20	21	22	23	24	25	26	27 and over <sup>1</sup>	
Frequency	15	7	11	14	5	4	3	4	4	3	4	2	9	

Mean yield =  $7.12 \pm 0.115$  gm.  $\sigma = 5.425 \pm 0.08$ . Mode (by inspection) = 4.0 gm.  
 CV. =  $76.19 \pm 1.14$  per cent. Coefficient of skewness (on  $\sigma$ ) =  $+0.575$ .

The results are represented graphically in the following figure:—

FIG. 2.<sup>3</sup>

The outstanding feature of the variation of rubber-yield among the population examined is indicated by the high coefficient of variability (CV), and the marked positive skewness of the frequency curve.<sup>3</sup> This feature is the presence of an important

<sup>1</sup> Mean of this group, 35.74 g.

<sup>2</sup> From *The Annals of Botany* (Clarendon Press).

<sup>3</sup> It may be noticed that Grantham and Knapp (*Archief*, 1918, 2, 618) remark that the frequency curve referring to the individual rubber-yields in a population of 1361 trees examined by them showed considerable skewness. They state that the probable error in the monthly yields expressed as a percentage of the mean yield was 42.9 over a six-months' period, and 40.4 over a twelve-months' period. The age of the trees was five years. They do not give any detailed data for the yields from individual trees.

number of trees yielding amounts of rubber several times larger than the modal amount, and affording, in proportion to the size of the population, a large mass of material for the profitable exercise of selection.

It may be remarked, as indicating the character of the distribution of yield among the trees on what is presumably a normal area of plantation rubber, that 9.6 per cent. of the trees (trees giving twice the mean quantity or more) was on the average yielding 3.6 times as much rubber per tree as the remainder of the trees. On the one hand, 9.6 per cent. of the trees on the area were contributing 28 per cent. of the total yield. On the other hand, 13.7 per cent. (groups 0-2 g.) were contributing only 2.9 per cent. of the yield, and certainly were not repaying the cost of tapping. The largest yielders in the population were four trees giving the following yields per diem: 41.45, 41.56, 41.72, 42, 77 g.

Rutgers<sup>1</sup> gives data obtained by Hamaker for the distribution of yield among the individual trees of a population of 1467 trees on a plantation in Java. The data show a contrast between the high- and the low-yielding trees similar to that just mentioned; namely: at one extreme, 9.0 per cent. of the trees (trees giving 17 g. or more) produced 23.9 per cent. of the crop, and, at the other extreme, 27.3 per cent. of the trees (trees giving 0.5 g.) produced only 7.2 per cent. of the crop. The classification recorded by Rutgers is as follows<sup>2</sup>:—

TABLE IV

Class . . . . .	> 17 g.	8-17 g.	5-8 g.	0-5 g.
No. of trees . . . . .	131	536	368	401
Total yield per diem (kg.) .	3.3	7.1	2.4	1.0

Mean yield per tree = 9.1 g.

*Rubber-yield and the anatomy of the cortex.*—Observations made by Bryce and Campbell<sup>3</sup> showed that individual trees differed

<sup>1</sup> *Archief*, 1919, 3, 105.

<sup>2</sup> Rutgers also shows classifications of a similar character for populations of respectively 4217 and 5000 trees on estates in Sumatra. In these two cases, however, the classification was made on the volume of the latex and not on the weight of rubber—a procedure shown by the data in footnote 4, p. 5, to be impermissible, except possibly for very rough work. The general character of the distribution of yield over these populations is, however, essentially similar to that in the cases quoted above.

<sup>3</sup> *Dept. Agric. Ceylon, Bull.*, No. 30, 1917.

in the number of the rows of latex vessels contained in the cortex (bark). Bobiloff<sup>1</sup> has made some observations on the relation of the anatomical structure of the cortex of individual trees, as revealed by microscopical examination, and the rubber yield. Broadly speaking, the elements of the trunk outside the wood are, in succession: the cambium, the soft, inner cortex (containing the latex vessels arranged in concentric rows,<sup>2</sup> and having medullary rays running into them radially), the hard outer cortex (containing layers of "stone"<sup>3</sup> cells), the cork. For the purpose of studying the relation between the anatomy of the cortex and the yield of rubber, Bobiloff classified the cortex of a number of trees from four points of view, namely (1) the number of rows of latex vessels; (2) the completeness or incompleteness of the rows; (3) the relative proportion of the soft part of the cortex where stone cells are absent, to the hard part where stone cells are abundant; (4) the distribution of stone cells in the cortex. For the purpose of classification from the last point of view, he established five types; there being in Type I no penetration of stone cells into the soft part, and in Types II-V penetration to increasing extents.

The number of rows of latex vessels in the soft part of the cortex showed a marked parallelism with the rubber-yield. The greatest number of rows found in any tree in the group of good yielders was 34; and the smallest number in any tree in the group of poor yielders 2. In the good yielders the soft part generally was more than 0.5 of the hard part (maximum figure 0.79); in the poor yielders it was generally much less (minimum figure, 0.083). It was found that, although its classification from any single one of the above points of view was not sufficient to indicate the yielding capability of a tree, when the character of the cortex was decided by consideration of all of the above points of view, it had, speaking generally, a clearly-marked relationship to the yield. Although the yielding capability of a tree could not, from an examination of the cortex, be determined quantitatively, it could be stated whether it was good, mediocre or poor. Bobiloff gives data for 36 trees, grouped as 10 good yielders, 8 mediocre yielders, and 18 poor yielders. In order to illustrate the character of his results, without reproducing the

<sup>1</sup> *Archief*, 1918, 2, 488.

<sup>2</sup> The mean distance between the rows was found by Bryce and Campbell, in the case of twelve-year-old trees in Ceylon, to be at 2 ft. from the ground 0.22, and at 8 ft. from the ground 0.25 mm.

<sup>3</sup> Lignified.

whole of his data, mean values for each group have been calculated, and are shown in the following table.

TABLE V

	High yielders.	Mediocre yielders.	Poor yielders.
No. of rows of latex vessels . . .	24	5.7	3.6
No. of incomplete rows . . .	0.7	1.5	1.5
Type of distribution of stone cells .	3.4	1.5	1.33
Thickness of soft part (mm.) . . .	2.82	1.43	1.00
Thickness of hard part (mm.) . . .	5.45	4.83	5.00
Ratio of soft and hard parts . . .	0.52	0.30	0.20
Thickness of cortex . . . . .	8.36	6.37	6.15
Yield of rubber . . . . .	47.6	9.3	3.07

Bobiloff also found that the number of rows of latex vessels was very approximately the same in renewed cortex as in original cortex on the same tree. This indicates that the number of rows of latex vessels is characteristic for a given tree.

Knowledge of the fact that the anatomical structure of the bark is related to the yielding capability of the tree is not unlikely to prove of considerable practical value in regard to selection and breeding. The results of actual tapping trials must, it would appear, always remain the final criterion of yielding capability, but, owing to the circumstance that at least five years must elapse before the yielding capability of a new generation can be decided by this criterion, other criteria would be useful.

A few observations relative to such a supplementary criterion—namely, the amount of rubber *in situ* in the bark<sup>1</sup>—have been made by Tromp de Haas.<sup>2</sup> Samples of bark were taken from three trees, planted in 1883, which in five years' tapping (1903-7) had given the yields mentioned below. In Table VI are shown the amounts of rubber in the air-dried bark—(a) referred to the whole bark, (b) referred to the inner 2 mm. (The total thickness of the bark differed in the different samples.)

TABLE VI

Tree . . . . .	No. 20	No. 29	No. 27
Yield (g.) . . . . .	8,054	2,401	1,520
(a) per cent. . . . .	2.62	2.23	1.62
(b) " " . . . . .	16.08	12.26	7.29

<sup>1</sup> This criterion was suggested by practice in regard to cinchona, where selection is based on the analytical determination of the amount of alkaloid in the bark.

<sup>2</sup> "The Valuation of Para Rubber Trees by a Chemical Method," *Lects. on Rubber*, 1908, p. 173.

The differences between the trees in respect of the amount of rubber *in situ*, whether this last is calculated as in (a) or as in (b), are less marked than the differences between them in respect of rubber-yield. In view of this, and of the further consideration that the analytical process<sup>1</sup> by which the rubber in the bark was determined was accurate only within 0.5 per cent. of rubber, Tromp de Haas concluded that such a chemical method could not give exact information as to the yielding capabilities of trees.

In view of the more recent results of Bobiloff, mentioned above, it would, however, seem that such a chemical method has a rational basis; although it is unlikely that the amount of rubber *in situ* in the cortex of different trees is in the same ratio as the yielding capabilities of the different trees. The present author, as mentioned earlier elsewhere,<sup>2</sup> obtained distinctly encouraging results in some preliminary observations concerning the amount of rubber *in situ* under different circumstances. He found the amount of rubber *in situ* in renewing bark to be less than the amount in original bark, but to approximate to the latter as the period of renewal extended.<sup>3</sup> It is to be hoped that further observations will be made on the variation of the rubber *in situ* in different trees and under different conditions.

*Collection of selected seed.*—There is a certain difficulty in securing seeds the origin of which is definitely known as being a given selected tree. This arises from the circumstance that the seeds are often projected to considerable distances when the ripe capsules burst; so that the seeds lying on the ground under a given tree are not usually all derived from the tree in question. It has been observed, however, that the seeds from any one tree are exactly similar in appearance;<sup>4</sup> so that it is sufficient to secure one true sample from a tree<sup>5</sup> in order to be able, after a little practice, to pick out the seeds from that tree from among

<sup>1</sup> The bark was extracted with chloroform; the solvent was distilled off, and the residue of caoutchouc, resins, colouring matters, etc., was extracted with acetone several times, the acetone solution being decanted off after each extraction. The residue was again dissolved in chloroform; the solvent was removed by distillation, and the residue was again treated with acetone. Finally, the material was dried at 70–80° in carbon dioxide.

<sup>2</sup> *Plantation Problems of the Next Decade*, 1914.

<sup>3</sup> The approximation to the original rubber-content appeared to take place more quickly than the approximation to the original thickness.

<sup>4</sup> Whitby, *Ann. Bot.*, 1919, 31, 319. For a similar observation made in Brazil, cf. Cramer, *Rubber Recueil*, 1914, p. 12.

<sup>5</sup> By placing conical bags of wire-netting round a few ripening capsules, or by picking off a capsule which is near the point of burst, or by watching the trees on a hot afternoon at the period when the capsules are bursting in numbers.

those lying on the ground in its neighbourhood. The differences which the seeds from different trees exhibit in regard to tint, mottling and size<sup>1</sup> are very marked, but even more striking than such differences is the accuracy with which the tint, the mottle-pattern, and the shape, down to such peculiarities as slight striations on one side, are repeated in all the seeds from a given tree.

A few data obtained by Hamaker<sup>2</sup> for five small groups of trees, the trees in one of the groups (No. 5) being derived from a single parent-tree, and those in the other groups from different parent-trees, may be noticed, as showing the greater uniformity in yield among trees of the same origin than among trees of different origins.

TABLE VII

Group	1	2	3	4 <sup>3</sup>	5
No. of trees in group	20	20	10	10	25
Maximum percentage deviation from mean	+ 34, - 40	+ 131, - 50	+ 115, - 67	a. 1916 + 62, - 65	b. 1917 + 68, - 36
Mean of deviations either way	+ 7.6, - 7.8	+ 16.7, - 16.8	+ 21.6, - 21.6	+ 15.2, - 14.9	+ 12.9, - 13.5
					+ 37.8, - 37.6

It appears probable that cross-fertilization is general with *Hevea brasiliensis*. Self-fertilization is, however, possible; and fair crops of seeds of pure strains can be obtained by preventing the occurrence of cross-fertilization by netting the trees in or by taking other suitable measures. It has been suggested,<sup>4</sup> as a method of avoiding the crossing of good yielders with poor or mediocre yielders, that certain areas should be specially reserved for seed production, and that on such areas all except the good yielders should be removed. Naturally, such areas could not be very large; and it is questionable whether this method would be as good as a method which would allow of good yielders being selected for seed-production wherever they were found.<sup>5</sup>

#### GROWTH OF THE TREE

Under plantation conditions *Hevea brasiliensis* grows with remarkable rapidity. For example, it will be found that areas in the Malay Peninsula and in Sumatra planted with six-months'-

<sup>1</sup> For data on the weight and size see Sprecher, *Bull. du Jardin Botanique de Buitenzorg*, No. XIX, 1915.

<sup>2</sup> *Archief*, 1917, 1, 441.

<sup>3</sup> A comparison of the data for this group in 1916 and in 1917 may be noted as illustrating the approximate constancy, to which reference has already been made, in the relative yield of trees over a considerable period of time.

<sup>4</sup> Lock, *Rubber and Rubber Planting*, Cambridge, 1913.

<sup>5</sup> *Vide* Whitby, *Plantation Problems of the Next Decade*, Weltevreden, 1914.

old stumps show after four years a proportion of, say, 60 per cent. of trees with a girth of 18 in. or more at a height of 22 in. from the ground.<sup>1</sup> The girth just mentioned is in the neighbourhood of the standards usually adopted as showing that a tree is large enough for tapping.

It is the well-nigh universal practice to keep the plantations (estates) absolutely clean-weeded by hand-weeding.

On the areas first opened up the trees were planted at distances, such as 10 × 10 ft. or 14 × 14 ft., which are now recognized as being too small. With recognition of the fact that the tree requires more room than such planting distances give, wider planting was adopted; and the greater part of the Eastern area is planted at such distances as 20 ft. square (108 trees per acre) and 24 × 30 ft. quincunx (120 trees per acre). But, it is recognized, that even when the trees are spaced at distances such as those last mentioned, the number of trees per acre requires to be continually reduced, as an area becomes older, in order that the existing trees shall have the opportunity to develop satisfactory leaf systems and that the optimum yield of rubber and best bark renewal shall be obtained.<sup>2</sup> When planted at distances such as those last mentioned, the trees begin to show signs of interlocking of the branches of adjoining trees, one year, say, after the area has come into bearing.

*Thinning-out.*—One or two points regarding thinning-out may be mentioned here; without, however, any attempt being made to discuss the subject in all its aspects. The selection of trees for thinning-out has generally been made on the basis of the appearance of the trees, particularly in regard to trunk-girth and the character of the head, and of general considerations of spacing. The results noticed in the preceding section show, however, that the extent of variation in the yielding capabilities of the trees on a given area is likely to be such that thinning-out, if it is to have its best effects, must be based primarily on determination of the yielding capabilities of the individual trees.<sup>3</sup>

<sup>1</sup> The rate of growth is somewhat slower in Ceylon and Java. The rate of growth throughout the year and in different years has been studied by Petch in Ceylon (*Annals Roy. Bot. Gardens, Peradenya*, 1916, 6, 77, and by Keuchenius in Java (*Archief*, 1918, 2, 407). Both find the rate to vary during the year, and to be zero during some period of the year.

<sup>2</sup> For a good statement on general lines of the necessity for continually reducing the number of trees, see the paper by Skinner, the most prominent pioneer in the application of thinning-out (*Rep. Batavia*, 1914, p. 112).

<sup>3</sup> Considerations of spacing must, naturally, be given some weight. And—it may be mentioned—the desirability of allowing a certain margin of trees to compensate for losses by disease may make it seem desirable to

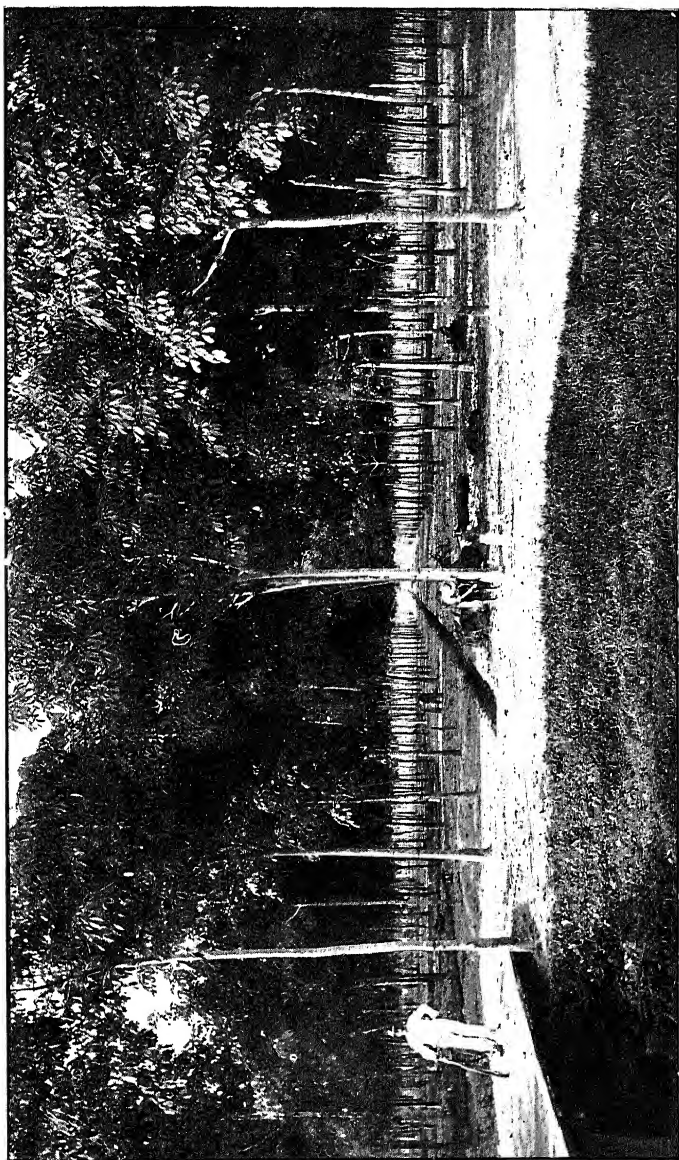


PLATE I. Young Trees in their first year of tapping.



Further, the presumption that a tree with a thicker trunk will give a larger yield than a tree with a thinner trunk is not sufficiently great to warrant trunk-girth being taken as a guide to the selection of trees for thinning-out to the extent which is now usual. Whitby<sup>1</sup> investigated the correlation between rubber-yield and trunk-girth in the group of 1011 seven-year-old trees to which reference has already been made (Table III), and found that, although there was a definite positive correlation between yield and girth, the extent of the correlation was not sufficient to justify very much emphasis being placed on girth when selecting trees for thinning-out. The girths in the following frequency table represent the mean of the girths at two points, viz. 22 and 36 in. from the ground.

TABLE VIII  
CORRELATION BETWEEN YIELD AND GIRTH IN A POPULATION OF 1011  
SEVEN-YEAR-OLD *HEVEA BRASILIENSIS*  
*Yields, grm. per diem.*

Girth, cm.	0-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	23-24	25-26	over 26	
50-52	1	1													2
53-56	5	3		1	1										12
57-60		11		5	3	1									29
61-64	14	15	2	6	3	2	1								49
65-68	13	24	16	17	13	4	2	1							70
69-72	16	30	25	17	17	5	2	2	1						106
73-76	17	28	19	17	14	14	2	2	1	1					114
77-80	17	36	32	21	14	11	8	4	1						146
81-84	16	27	29	23	8	6	6	6	6	2					127
85-88	13	28	21	10	8	9	2	2	3	3	1				114
89-92	8	17	18	19	9	6	1	1	6	3					91
93-96	5	9	10	12	9	4	3	3	1		3				60
97-100	3	8	9	4	5	5	5	3	3	1					49
101-104	2	2	5	2	3	3	1	1	1						20
105-108				3	3	2	2								8
109-124	1	2	2	2	1					1	1				14
	139	241	199	154	83	71	39	22	25	9	7	7	6	9	1011

$$r = +0.260 \pm 0.020.^3$$

fix the number of trees to be thinned-out at any given time at a somewhat lower figure than would, apart from the possibility of loss by disease, be the optimum figure.

For data concerning the effects of thinning-out in maintaining or improving the yield, see Skinner (*loc. cit.*), Patterson (*Tropical Agriculturalist*, 1916, 47, 44), Arens (*Archief*, 1917, 1, 234), and, particularly, Rutgers (*Archief*, 1919, 3, 105). The last gives some data showing that within a given period bark renewed to a greater thickness on thinned-out than on corresponding non-thinned-out areas.

<sup>1</sup> *Ann. Bot.*, 1919, 31, 319.

<sup>2</sup> Mean girth,  $80.30 \pm 0.25$  cm.

<sup>3</sup> Complete correlation would be indicated by  $r = 1$ ; the complete absence of correlation by  $r = 0$ .

## SOILS AND MANURING

Speaking broadly, the soils upon which rubber shows its vigorous growth on plantations do not appear to chemical analysis as, from the standpoint of agriculture in the temperate regions, rich.<sup>1</sup> The question as to whether manuring will give a paying increase in the rubber-yield, and, if so, under what circumstances it will give such an increase, and of what its character should be under such circumstances, has hitherto been the subject of few, if any, convincing experiments. The results of experiments on the manuring of rubber trees have been published at various times, but, owing to the failure of the experiments in most cases to conform to the canons (discussed below, in connection with tapping) of reliable field experimentation, do not for the most part carry conviction.<sup>2</sup> Manuring has been carried out to only a small extent in all the plantation rubber-growing countries, with the exception of Ceylon. In the latter country, where the soil has for a large part been under cultivation for longer periods than elsewhere, manuring has been largely accepted as a part of estate routine. But there does not appear to be any conclusive evidence that it gives paying results<sup>3</sup>; although it is not impossible that it may do so.

Speaking very generally, the soils upon which rubber is grown, like most tropical soils, are markedly deficient in lime. Barrow-cliff,<sup>4</sup> who determined the lime absorption of typical Malayan rubber soils, found the "lime requirement" of the undulating land inland to be 2-3 tons, and of the clays and peaty clays on the coast 5-6.5 tons per acre. And the indication of a number of field experiments, which, however, require confirmation, has been that the addition of lime (in quantities short of the full "lime requirement") has a distinctly good effect on the growth of rubber and the yield of latex. Gallagher<sup>5</sup> concluded, from experiments in Sumatra, that much greater increases in girth

<sup>1</sup> For data on the composition of rubber soils, see H. Wright, *Hevea brasiliensis*, 4th edition, London, 1912; Mohr, *Rubber Recueil*, 1914, p. 167; Grantham, *Agric. Bull. F.M.S.*, 1916, 4, 114, 247; C. H. Wright, *Rubber Soils of Fiji*, 1917.

<sup>2</sup> For published results relative to the manuring of rubber, see *Agric. Bull. F.M.S.*, 1913, 1, 194; 1914, 2, 88; 1915, 3, 9, 111; 1916, 4, 105, 125, 373; I. R. J., 1918, 683; *Dept. Agric. Ceylon Bull.*, Nos. 18 and 36.

<sup>3</sup> The author could discover no such evidence on a visit to Ceylon in 1914. Nor do the experiments recorded in *Dept. Agric. Ceylon Bull.*, Nos. 18 and 36, appear to afford any.

<sup>4</sup> "The Acidity of Malayan Soils," *Agric. Bull. F.M.S.*, 1914, 3, 45.

<sup>5</sup> *Rep. Batavia*, 1914, p. 71.

in young trees (trees 1 year 9 months old at the beginning of the experiments) were to be brought about by artificially inducing branching than by liming and the application of complete manure.<sup>1</sup>

The above remarks on manuring are not to be read as implying that manuring is not likely to be of much value in rubber growing, but, rather, as pointing to the need for more extensive and exact experiments (cf. section on Field Experimentation with Rubber). Until the results of such experiments are available, it would seem that properly-conducted thinning-out (and, probably, induced branching) is in most cases more deserving of close, practical attention, as a means to yield improvement, than is the application of manures.

#### TAPPING

The extraction of latex from the tree is generally performed by paring<sup>2</sup> the bark away in a systematic manner. One or more oblique cuts are made in the bark; and at intervals, usually of one or of two days, a thin paring of bark is removed along the cut by means of a gouge, a simple instrument on the lines of a farrier's knife, or a kind of chisel provided with sides. Tapping is performed early in the morning. Each paring has the effect of opening up the ends of the latex vessels. Under the influence of root pressure, latex oozes out for, say, one hour. The latex runs down the cut, and is conducted from the lower end of the cut down a shallow vertical channel which has been cut in the bark to a small spout which has been stuck into the trunk a few inches from the ground. The latex drips into stout,

<sup>1</sup> The present writer is inclined to regard the artificial inducement of branching (by stripping the leaves or other means) as a very valuable plantation procedure. It tends to produce trees with large heads and short, thick trunks. Such trees must be regarded as more suitable from the point of view of rubber yielding than the trees with long trunks, and, by comparison, "spindly" in character, which were grown on the areas opened up in the early days of plantations. It is safe to say, from our present-day knowledge of the anatomy of the tree and of tapping principles, that no tapping system in the future is likely to demand a tall trunk.

<sup>2</sup> Methods of extracting latex by pricking—*incision* methods, as contrasted with the usual *excision* methods—have been proposed at various times, but, for a variety of reasons, have not met with any wide acceptance. Campbell (*Dept. Agric. Ceylon, Bull.*, No. 19, 1915) finds that the effect of pricking on the local withdrawal of food reserves is not less, but rather more than the effect of paring. Spring (*Rubber Recueil*, 1914, 303) found pricking to give the same yield of rubber as paring a single cut on a quarter of the circumference. He did not find the serrated knife to injure the trees. He found the cost of tapping by pricking to be high.

clean, handle-less cups of porcelain or glass. On the average the parings are about  $\frac{1}{25}$  in. thick; so that, in the case of daily tapping, an amount of bark measuring about 14 in. vertically is excised in the course of a year of 350 tapping days.

The flow of latex from a new cut does not establish itself immediately. During the first few tappings the yield of latex is small. It reaches its normal proportions only after tapping has been repeated several times. The phenomenon here remarked has been termed "wound response." In a statistical inquiry of considerable dimensions into the relationship of wound response to rainfall, the author found that the yield of latex establishes itself much more slowly in dry weather than in wet weather or immediately after wet weather. In some cases four to six weeks' daily tapping was required in dry weather, whereas the period was only one week in favourable weather. It was concluded that in the Malay Peninsula the months of June and July were most likely to be unfavourable to wound response.

Arisz<sup>1</sup> has indicated an interesting method of investigating the point of origin of the latex obtained from a given cut, depending upon determinations of the depression of freezing-point produced by the constituents of the latex (principally salts, quebrachitol and sugars) responsible for the tension in the laticiferous vessels. Arisz finds that, when the latex from a cut is collected in (two, three or four) parts, later parts, although similar in total-solid-content to earlier parts, produce noticeably smaller freezing-point depressions than do earlier parts. Further, the latex obtained from a cut on the roots, although similar in total-solid-content, produced a smaller freezing-point depression than latex from an ordinary cut on the trunk. The difference in freezing-point depression between latex from two cuts so situated became even more marked when the root cut was opened only after the ordinary cut (height, 30 cm.) had been exuding for some time; the depressions produced by the latex from an ordinary cut and from a root cut being in these circumstances in one experiment quoted  $0.830^{\circ}$  and  $0.627^{\circ}$  respectively. The conclusion was indicated that the latex obtained from a given cut flows up to the cut from the bark below it; and that in the case of a cut at a level of about one foot from the ground the latex is derived largely from the root trunk and the roots.

This conclusion found support in the following observations :  
(a) Latex derived from a cut higher on the trunk (viz. at 3.5 m.)

<sup>1</sup> *Archief*, 1918, 2, 347.



PLATE II. Trees tapped by "V" cuts.



PLATE III. Older tree tapped on renewed bark.

than the ordinary cut, although somewhat lower in total-solid-content, gave a greater freezing-point depression than latex from the ordinary cut. Hence, it is improbable that latex from the ordinary cut is derived from higher in the trunk. Like the latex from the ordinary cut, that from the higher cut showed, when collected in two parts, a smaller freezing-point depression in its second than in its first part. (b) When, by a suitable arrangement of dams, the latex from the three equal lengths into which a cut was divided was collected separately, the latex from the middle length was found to give a noticeably smaller freezing-point depression than the latex from the outer lengths. This result is explicable on the assumption that the middle part of the cut receives almost all its latex from the roots, whereas the outer parts derive some of their latex from a flow of latex from the latex vessels just outside the ends of the cut.

*Tapping systems.*—Throughout the history of the Eastern plantations there has been a very marked tendency to adopt more and more conservative systems of tapping, *i. e.* systems involving the excision of less and less bark. The V system, in which two cuts, each covering a quarter of the circumference, were arranged in the shape of a V, was until comparatively recently the system which was perhaps most in vogue. Where the tapping was conducted on alternate days only, two V's, one above the other, might be used. Other arrangements, under which the bark consumption was similar to that under the V system, were (a) two superposed cuts on the same quarter of the trunk, (b) two cuts, each cut being on an opposite quarter of the trunk, (c) etcetera. The present tendency is towards the adoption of still more conservative systems, particularly of a single cut on one-third or one-quarter of the circumference. It is not proposed to examine here the relative merits with regard to the yield of rubber and the bark renewal of the different systems which are now in vogue or have been proposed; because (cf. the section later on "Field Experimentation with *Hevea*"), although available experimental results enable judgment to be passed for practical purposes on the relative merits of tapping systems which differ markedly in their effects, they do not for the most part enable any exact or final judgment to be rendered in the case of systems which differ less markedly. A number of points, at least some of which have been established with a degree of conclusiveness such that they may perhaps rank as tapping principles, may, however, be noticed.

(1) *Height of the cut.*—The higher a cut is situated on the trunk, the smaller is its yield of rubber.

The effect of the distance of the cut from the ground on the yield of rubber is particularly marked over the lowest portion of the trunk; the difference in yield obtained from a cut at a height of, say, one foot, and a cut at a height of, say, two feet, being much greater than the difference between cuts one foot apart at higher levels. This is one of the most important considerations in devising a tapping system. From the point of view of the magnitude of the rubber-yield, a tapping system should have the effect of keeping the cuts throughout as near to the ground as possible.

This general conclusion has been illustrated in many tapping trials. As an example of such an illustration, reference may be made to a trial with which the author was associated. Two adjoining groups of 600 trees had for four years been tapped with V cuts. In the fifth year of tapping, one group was tapped with a V on the four-years'-renewed bark on the lowest section of the trunk (from 22 in. downwards), the other group was tapped with a V on the section of the trunk above the already-tapped sections (say, from 54 in. downwards). In their fourth year of tapping the groups gave approximately equal yields. In their fifth year, although the group being tapped by the lower cut was being tapped on renewed bark, whereas the group being tapped by the upper cut was being tapped on original bark, the yield from the former group was more than twice that from the latter.<sup>1</sup> When the two groups were reversed as regards tapping position, the relation between their yields was also reversed.

An investigation by Bryce and Campbell<sup>2</sup> into the number of latex vessels at different levels on the trunk has revealed an anatomical reason for the observed relation between the height of the tapping cut and the yield of rubber. They found that the number of rows of latex vessels in the bast diminished as the trunk was ascended; the diminution being particularly rapid over the lower part of the trunk (up to, say, four feet)—which is the part usually employed for tapping. From the results obtained by them from the examination of fourteen trees, it may be calculated that, for this particular collection of trees, the mean

<sup>1</sup> And the proportion of naturally-coagulated rubber (lump) from the former group was only about 20 per cent. of that from the latter.

For other data on the influence of the height of the cut on the yield, see, e. g. *Archief*, 1917, 1, 83.

<sup>2</sup> *Loc. cit.*

numbers of complete rows of latex vessels at one foot and at four feet respectively were 9 and 4.7 and of (complete + incomplete) rows 12 and 6.5. Such differences in the anatomy of the bark at different levels do not necessarily account completely for the fall in yield with increasing height of the cut. The influence of root pressure would also appear to demand consideration.

(2) *Number of cuts.*—The yield does not increase in proportion to increase in the number of tapping cuts.

This follows, of course, from the conclusion noted under (1). It is also a consequence of the fact (cf. the results of Arisz, p. 16) that a cut placed over another has the area of bark which it can possibly drain limited by the cut below it. In the early days it was often attempted to increase the yield by tapping a comparatively large number of cuts, at different levels, arranged in herring-bone or half-herring-bone fashion. But it is now recognized that such a series increases the yield over that given by a single cut at a low level to only a comparatively small extent, and at the same time consumes bark which would be of greater value in subsequent years; so that economical considerations do not recommend it.

In an experiment made by Lock,<sup>1</sup> in which a group of twenty-nine trees was tapped with six V cuts each placed one foot above the cut below, the following yields per cut in nearly six months' tapping were obtained: 67,942, 25,998, 22,353, 18,773, 16,606 cc. The cuts are given in succession; the lowest, which was one foot from the ground, being given first. The percentage of rubber in the latex was slightly higher in the case of the lower than in the case of the higher cuts. In various tapping trials two cuts have been reported as giving a yield only 10–30 per cent. greater than the lower cut alone.<sup>2</sup>

De Jong<sup>3</sup> has made some observations on the influence of tapping a lower cut on the yield from a cut above it. When the upper cut was opened immediately after the lower one, the flow of latex from it was noticeably influenced by the lower cut, if the latter was 35 cm., but not if it was 75 cm. or 1 m. below it. When the upper cut was opened one hour after the lower one, the flow of latex from the former was influenced even with the larger distances between the cuts.

<sup>1</sup> *Rubber and Rubber Planting*, Cambridge, 1913, p. 80.

<sup>2</sup> For the results of tapping trials bearing on the relation of the number of the cuts to the yield, see *Agric. Bull. F.M.S.*, 1, 440; *Teysmannia*, 1917, 30; *Tropical Agriculturalist*, 1918, 50, 231.

<sup>3</sup> *Archief*, 1917, 1, 384, 400.



(3) *Length of the cut.*—The yield does not increase in proportion to increase in the length of the cut.

This would appear to be due to the existence of a lateral flow towards an opened tapping cut in addition to the longitudinal flow (cf. Arisz, p. 16).<sup>1</sup> De Jong<sup>2</sup> found that when two cuts, placed at the same level on a given tree, and separated by a horizontal distance of 5 cm., were tapped immediately after one another, neither cut influenced the yield from the other; but that when an interval of one hour elapsed between the openings the yield of the cut tapped last was reduced.

The following ratios between the yields from cuts on one-quarter, one-third and one-half of the circumference (ratio of the length of the cuts : 100:133:200) have been reported as the result of various tapping trials:—

100:117:140; 100:116:135.5; 100:117:137.5<sup>3</sup>; 100:116.<sup>4</sup>

(4) *The tapping interval.*—With increase in the interval between tapplings, the yield per tapping in general increases, but the total yield diminishes. In particular, tapping on alternate days gives a greater yield of rubber per tapping but a smaller total yield than tapping daily. There is a tendency to excise more bark per tapping when the tapping is done on alternate days than when it is done daily.

A collation, made by Corporaal,<sup>5</sup> of the results of trials reported by eleven different authors shows (excluding a low figure of 39) figures ranging from 54 to 75, with a mean of 60, as the yield obtained by alternate-day tapping expressed as a percentage of the yield obtained by daily tapping.<sup>6</sup> A collation of the results of three trials in which the bark consumption was noted places the latter at from 51 to 75 per cent. (mean, 62 per cent.) in alternate-day tapping of the consumption in daily tapping. Campbell<sup>7</sup> concludes from measurements of bark thickness

<sup>1</sup> For a different and largely opposed view, cf. Bateson, *Dept. Agric. F.M.S. Bull.*, No. 23, 32-3.

<sup>2</sup> *Archief*, 1917, 1, 384, 400.

<sup>3</sup> The first three sets are the results obtained in three successive years during which the trial was continued. De Jong, *Teysmannia*, 1916, 520; *Archief*, 1918, 2, 152.

<sup>4</sup> Results of trial over three years. *Archief*, 1918, 2, 199. For other results bearing on the same point, cf. *Archief*, 1918, 140; *Agric. Bull. F.M.S.*, 1, 440.

<sup>5</sup> *Archief*, 1918, 2, 141.

<sup>6</sup> A trial reported subsequently (*Archief*, 1918, 2, 199) gives the figure 69 per cent.

<sup>7</sup> *Dept. Agric. Ceylon Bull.*, No. 33 (1917).

that trees tapped daily throughout the year show poorer bark renewal than trees tapped at longer intervals. The measurements were made in Ceylon, where alternate-day tapping is commonly practised.

The question as to whether the frequency of tapping is a factor in the production of "brown bast" is still under discussion.<sup>1</sup>

(5) *Obliquity of the cut*.—In some trees of *Hevea brasiliensis* the latex vessels slope (upwards) to the right at an angle roughly 5° to the vertical. De Jong concluded from experiments on small groups of trees on which cuts were placed, at an inclination of 45°, on the right and on the left of the vertical channel, and on which, in order to eliminate possible inaccuracies due to variation in the depth of tapping, tapping was done to the wood, that, as would be expected if the latex vessels had the inclination just mentioned, left cuts gave more than right cuts. In de Jong's first experiments<sup>2</sup> the advantage of the left cut over the right was on the average 8 per cent. In a more recent experiment<sup>3</sup> it was 14 per cent.

*Tapping and food reserves*.—Fitting<sup>4</sup> found that tapping trees on the drastic system of the full-spiral or of the half-herring-bone (with six cuts) led to a serious depletion of the food reserves, as represented by starch and reducing sugar, in the bark and wood. He came to the conclusion that tapping was equivalent to complete or partial girdling of the tree. In subsequent observations made by Simon,<sup>5</sup> and in more extensive subsequent observations made by Bateson,<sup>6</sup> and, especially, by Campbell,<sup>7</sup> the effect of tapping on the food reserves was found to be much less severe than that indicated by Fitting.

It has been found that the effect of reasonably conservative tapping in withdrawing food reserves is in all cases purely local. Speaking generally, it is found that the outer layers of the wood immediately under a recently-tapped area of bark are half-full of starch to a depth (inwards) of 2.5 mm., and are empty only

<sup>1</sup> "Brown bast," an abnormal or diseased condition of the bark, is causing some concern on the plantations. It is at present generally regarded as physiological in origin.

<sup>2</sup> *Archief*, 1917, 1, 362.

<sup>3</sup> *Archief*, 1919, 3, 1. Rutgers (*Archief*, 1918, 2, 199) finds no advantage in favour of the left cut. For de Jong's reply, see *ibid.*, 327.

<sup>4</sup> *Tropenpflanzer*, 1909, 13, Beih. Nr. 2, 1-43. (Eng. trans.: *Physiological Principles for Determining the Value of Rubber-Tapping Methods*, London and Colombo, 1909, p. 51.)

<sup>5</sup> *Tropenpflanzer*, 1913, 17, 63, 119, 181.

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Dept. Agric. Ceylon Bull.*, Nos. 16, 19, 22 (1915).

over a narrow strip, 1 mm. deep, under the tapping cut. It now appears probable that tapping cannot justly be regarded as equivalent to girdling: that food transport from the leaves over tapped portions of the circumference takes place within the thin inner layer of bark which is normally left untouched in tapping.

It has been found that, although no withdrawal of starch reserves takes place during the period of defoliation and while the trees remain leafless (the period of "wintering"), there is a comparatively large withdrawal of starch during the subsequent period, when the new leaves are attaining their full size. The starch disappears from the bark and, to a depth of 5-10 mm., from the wood. Bateson, working in the Malay States, found that a period of several months was required in order to replenish the starch reserve following this withdrawal; and he considered that, in view of this, and of the fact that the depletion produced by tapping is only slight, cessation of tapping for two or three weeks after "wintering" would have no appreciable effect on the rate of replenishment and need not be practised.<sup>1</sup> Campbell, working in Ceylon, found that recovery of starch reserves *began* to take place within three weeks of the time that the new leaves were fully formed; and that recovery continued until June (say, until the lapse of rather more than two months). He considered that tapping should be discontinued for one month or more from the time when the leaves are falling. Rutgers,<sup>2</sup> writing from Sumatra, points out that the most severe case of wintering takes only one-sixth of the starch reserves. He considers that, as tapping takes only a slight amount, there is no reason, from a physiological point of view, for stopping tapping.<sup>3</sup>

<sup>1</sup> He considered that the effects of "wintering" do not form a special problem to be met by special means; but that, as they are spread over a long period, they merely form part of the general problem—to devise a method of tapping which, over a period of years, will not be so exhaustive to the tree as to check its full development.

<sup>2</sup> *Archief*, 1917, 1, 95.

<sup>3</sup> Climatic conditions must be borne in mind in considering the advisability of stopping tapping during the wintering period.

In Ceylon it is the almost universal practice to stop tapping for, say, four to six weeks. The period of wintering usually coincides with a period of dry weather, during which the yield would in any case be poor.

In Ceylon the distribution of the rainfall and of the crop throughout the year is less uniform than in the Malay Peninsula (*vide* graphs I.R.J., 1916, 444). In Southern India the distribution of the rainfall throughout the year may be even less uniform (*cf.* Lock, *op. cit.*, 73). For data relative to the variation in rainfall and crop in Java, see ten Houste de Lange, *Archief*, 1918, 2, 105.

## FUNCTION OF LATEX

The question as to what is the significance of latex in the physiological economy of laticiferous plants in general and of *Hevea brasiliensis* in particular is, clearly, a question fundamental to the rational exploitation of rubber-producing plants. Yet, despite the fact that many investigations have been made with the object of throwing light on the function of the latex in laticiferous plants, it does not appear that any adequate understanding of the matter is yet in sight.<sup>1</sup> The present state of knowledge of this question is not such as to justify treatment of the subject in any detail.<sup>2</sup>

The most important question, stated broadly, relative to the function of latex is whether latex is an alimentary or an excretory product. Those who have regarded it as important to the nourishment of the tree have adopted standpoints differing considerably among themselves. Some botanists have viewed latex as, substantially, circulating sap, conducting foodstuffs. The chief protagonist of the view that the laticiferous tubes are analogous to sieve tubes has been Haberlandt.<sup>3</sup> A recent inves-

<sup>1</sup> Kniep, himself a worker on the subject, remarks (*Rubber Recueil*, 1914, 63): "Unter den pflanzlichen Zell- und Gewebearten gibt es wenige, über deren physiologischen Funktion so wenig gesichertes Tatsachenmaterial vorliegt wie über die Milchröhren und Milchgefäße. An Arbeiten darüber und an Hypothesen fehlt es freilich nicht. Doch sind die Ansichten der einzelnen Autoren und der Wert ihrer Beweisgründe so verschiedenartig, dass es unmöglich ist, ein einheitliches Gesamtbild von der Physiologie des Latex zu entwerfen." And Went remarks (*Rep. Batavia*, XXIV): "What do we really know up till now about the functions of latex? . . . I have taken the trouble to read up the whole of the botanical literature on latex and I must declare that I could not give a satisfactory answer. The formation and development of the tubes containing the latex is pretty well known, although our knowledge in this respect also presents large gaps, but the latex itself is still so little known to us that we cannot even fully identify it with the content of other plant cells. And its functions? I have the greatest admiration for the attempts which have now and then been made by investigators like Hanstein, Faivre, Molisch, Kniep, Bruschi and various others, but the question is just as mysterious as when the investigations began."

<sup>2</sup> For reviews of our present knowledge of the physiology of latex and for bibliographies relative to the subject, *vide* Koketsu, *Jour. Coll. Sc.*, Tokyo, 1913-15, 35, Article 6, p. 57; *Bot. Mag.*, Tokyo, 1913, 27, 133; Kniep, *loc. cit.*; Bobiloff, *Archief*, 1918, 2, 281.

Most investigations of laticiferous plants hitherto made have been conducted in Europe. Now that the more intensive investigation of the physiology of latex is being taken up in the tropics by workers for whom it will form the chief task, a more rapid approach to a solution may be looked for.

<sup>3</sup> *Sitzungsber. Wien*, 1883, 87 (Ab. I), 51; *Physiologische Pflanzenanatomie*, 4. Aufl., Leipzig, 1909.

tigation conducted with *Hevea brasiliensis* by Bobiloff<sup>1</sup> appears to demonstrate with some conclusiveness that this standpoint is, at all events in the case of *Hevea*, impermissible. Bobiloff finds that at the base of the petiole of the mature leaf of *Hevea* there is a layer of crystals of calcium oxalate which has the effect of preventing any circulation of latex from the leaves to the stem. This observation shows, further, that the latex obtained by tapping the stem cannot have its origin in the leaves. Observations of Kniep, Koketsu and others with other plants are also opposed to the view that the laticiferous system is a means of transporting foodstuffs. Other botanists, who, from other points of view, not involving the idea of a circulation of latex, consider latex to be of value in the nourishment of the plant, and who regard the latex as a whole or some of its constituents (carbohydrates, proteins) as habitual or reserve food for the plant, are Schullerus, Molisch,<sup>2</sup> Faivre, Bruschi, Bernard<sup>3</sup> and others. Vernet,<sup>4</sup> from observations on *Hevea brasiliensis*, has advanced some arguments of considerable force in favour of the view that latex is a food indispensable to the tree.

Such chemists as have written on the function of latex have for the most part been inclined to regard it as that of a foodstuff, and have been concerned to consider possible reactions by which under the conditions of plant life the hydrocarbon caoutchouc could, on the one hand, be formed, and, on the other hand, be converted into soluble products capable of utilization by the tree. It must be confessed, however, that the treatment of the physiology of latex in its chemical aspects has been almost entirely speculative, owing to the inadequacy of germane experimental data. Harries, whose work on the constitution of the caoutchouc molecule<sup>5</sup> is well known, found caoutchouc to be attacked readily by ozone, with the production of an ozonide which on hydrolysis gave prominently levulinic aldehyde, a substance, containing the grouping  $C_5H_8$ , which is closely related to the pentoses, and which can be obtained from carbohydrates, such as starch, by the action of hydrochloric acid. He also found that the ring of  $\alpha$ -methyl furane, a body which can readily

<sup>1</sup> *Archief*, 1918, 2, 737.

<sup>2</sup> *Studien über den Milch- und Schleimsaft*, Jena, 1901.

<sup>3</sup> *Ann. Jard. Bot. de Buitenzorg*, 1910, 3, suppl., 235; *Teysmannia*, 1918, 29, 523 (vide *Archief*, 1919, 3, 179).

<sup>4</sup> *Le Caoutchouc*, 1910, 7, 3808.

<sup>5</sup> A discussion of the question of the structure of the caoutchouc molecule is beyond the scope of the present volume. For recent views on the subject, see papers by Harries, Pickles and Ostromyslensky.

be obtained from carbohydrates, is easily opened, with the formation of levulinic aldehyde. Harries supposes that caoutchouc is formed by the condensation *in statu nascendi* of  $C_5H_8$ -residues derived from the reduction of sugars, chiefly pentoses. Harries, indeed, supposes that not only caoutchouc, but also all the terpenes are physiologically related on similar lines to the sugars.

Dubosc and Luttringer<sup>1</sup> suggest that it is possible that methyl derivatives of butadiene—from which, according to a suggestion of Hoffmann (1912), rubber arises in the plant—are derived in the plant from the inositol or its derivatives found in many latices; the latter compounds having been formed from starch or cellulose. Spence,<sup>2</sup> on the general ground that an oxidase or oxidases exist in the latex, suggested that caoutchouc, acting as a reserve food, was broken down by oxidases in the plant into simpler, assimilable substances. The presence in the latex of an enzyme capable of oxidising caoutchouc was not, however, demonstrated; the oxidase or oxidases present were recognized only as bringing about the darkening of coagulated rubber.<sup>3</sup> Whitby<sup>4</sup> encountered on a plantation, at a time when the trees were "wintering" and were suffering from drought, a number of samples of rubber in which there was going on at ordinary temperature a rapid oxidation of the caoutchouc into a product ("resin") soluble in acetone.<sup>5</sup> (Cf. section on Tackiness and Oxidation, p. 100.) Indications were obtained that this conversion was due to an organic (presumably enzymic) agency, but it was not conclusively established that such was the case. It is, however, in any case, well known that under the influence of a suitable catalyst caoutchouc can readily be converted into an oxygenated product known as "resin." It is less difficult to conceive the breakdown of such a product than of the hydrocarbon caoutchouc into substances assimilable by the tree. And Whitby put forward the suggestion that "resin" represented an intermediate stage in a breakdown of caoutchouc into assimilable substances; the quantity of resin in relation to caoutchouc

<sup>1</sup> *Le Caoutchouc, sa Chimie nouvelle, ses Synthèses*, Paris, 1913.

<sup>2</sup> *Biochem. Jour.*, 1908, **3**, 165.

<sup>3</sup> By, it was supposed, acting on the carbohydrate complex of the latex protein. (Spence, *Lects. on Rubber*, 1908, 198.)

<sup>4</sup> *Koll. Zeit.*, 1913, **12**, 147.

<sup>5</sup> In this connection it is of interest to note that Kerbosch (see p. 70, Chap. II) observed a marked change in the latex, in regard to its content of acetaldehyde, at the time of wintering. At this time acetaldehyde was found to disappear from the latex almost entirely.

in the latex present in the laticiferous vessels representing possibly an equilibrium position between anabolism and katabolism. Spence<sup>1</sup> also has drawn attention to a possible relation between caoutchouc and latex resins in regard to metabolism.

A not inconsiderable number of authors have expressed the belief that latex is not concerned in the nourishment of the tree. The grounds upon which an alimentary function has been denied to latex have been various. In some cases (*e. g.* Kniep, Warming, Parkin) they have been experimental. In other cases they have been such general considerations as: (a) the fact that the laticiferous system does not take the place of any structural arrangements present in non-laticiferous plants, but is, as it were, something added on, which, therefore, can be regarded as non-essential to the nourishment of the tree<sup>2</sup>; (b) the (supposed) character of the latex vessels of forming a closed system without connection with the other tissues, marking it out as a place for the reception of an excretion; (c) the difficulty of conceiving the utilization for alimentary purposes of an inert, hydrocarbon material such as caoutchouc, and the smallness of the amounts of recognized foodstuffs (carbohydrates, proteins).

Various investigators have ascribed ecological functions to latex and have placed emphasis upon such functions. As Kniep, himself one of such investigators, has pointed out,<sup>3</sup> the question of the ecological significance of latex is distinct from the question of its significance in metabolism. In the view of Warming,<sup>4</sup> the chief function of latex is to act as reserve of water for the protection of the plant against drought. This view

<sup>1</sup> *Lects. on Rubber*, 1908, 194.

<sup>2</sup> A permissible speculation with regard to the puzzling circumstance of the existence of classes of plants, which appear to possess all the normal structures of a plant, and to be able to exist by virtue of such structures alone, and which yet possess a system (the laticiferous system) added on, as it were, to the normal structures and apparently non-essential, is that which would view the place of latex in the economy of rubber plants as analogous to the relation of insects to the so-called carnivorous plants. Plants of the latter class can live and even thrive without insects, but they lead a more vigorous existence if they are fed on insects than if they fail to get such nutriment. It may be that, without latex, rubber plants could live and even thrive, but that, with latex, they lead a more vigorous existence than without it. The favourable influence of the protein food which insects supply to carnivorous plants is chiefly dependent, it has been suggested, not on the larger amount in which but on the form in which the food is made available to the plant. (Whitby, *Plantation Problems of the Next Decade*, 1914, p. 29.)

<sup>3</sup> *Rubber Recueil*, 1914, p. 85.

<sup>4</sup> *Ökologische Pflanzengeographie*, 2 Aufl., 1902; *Bot. Gaz.*, 1899, **37**, 1; *Ecology of Plants*, Oxford, 1909, p. 125.

finds supporters in Parkin,<sup>1</sup> Olsson-Seffer<sup>2</sup> and others; but, in view of the nature of the climatic conditions under which most rubber plants grow, and of the readiness with which the water-content of latex responds to changes in external conditions, the supposed function would not appear to be important.<sup>3</sup> Stahl,<sup>4</sup> Kniep,<sup>5</sup> H. de Vries,<sup>6</sup> Koketsu<sup>7</sup> and others regard latex as, prominently, a protective material against the effects of wounds and the attacks of insects and fungi. The view that at all events a function of latex is a protective one has received very wide acceptance.<sup>8</sup> Cases have, however, been reported at various times of boring-beetles which can penetrate the bark of *Hevea brasiliensis* without being killed by the latex<sup>9</sup> and of latex-drinking beetles.<sup>10</sup> And Sharples<sup>11</sup> has recently reported some experiments which point to the conclusion that, not the laticiferous layer, but the corky integument, protects *Hevea brasiliensis* against attacks of insects and fungi. A group of well-grown, untapped, five-year-old plantation trees, in a situation which was not favourable to insect attack, was divided into a number of blocks. On some blocks the trunks were heavily scraped, the green cork-cambium being removed; on others they were lightly scraped, the green cork-cambium being left. One block acted as a control. It was found that, while none of the control trees was attacked, a large proportion of the heavily-scraped trees and a smaller proportion of the lightly-scraped trees were attacked by boring beetles. The rapidity of attack was striking, borers being active on the tree first affected within four days.<sup>12</sup> Sharples states that his field experience is in agreement with the above experiment. He has observed, *e. g.*, that, when trees are injured by leaf fires, borers often get quickly to work on the scorched portions of the trees. "In every case a copious exudation of latex was noticeable from the bore holes, but this did not prevent the entry of the insects."

Regarding the question as to where in the plant latex is formed, Bateson<sup>13</sup> and, particularly, Bobiloff<sup>14</sup> have advanced good

<sup>1</sup> *Ann. Bot.*, 1900, **14**, 193.

<sup>2</sup> *Agric. Bull. Straits Settlements and F.M.S.*, 1907, **6**, 1.

<sup>3</sup> Cf. Petch, *The Physiology and Diseases of Hevea brasiliensis*, London, 1911, p. 43.

<sup>4</sup> *Flora*, 1905, **94**, 129.

<sup>5</sup> *Pflanzen und Schmecken*, Jena, 1888.

<sup>6</sup> *Landwirtschr. Jahrb.*, 1881, **10**, 687.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> Cf., *e. g.* Lock, *op. cit.*, p. 52.

<sup>9</sup> Vernet.

<sup>10</sup> Keuchenius, *Archief*, 1917, **1**, 147.

<sup>11</sup> *Ann. Bot.*, 1918, **30**, 247.

<sup>12</sup> One of the trees was attacked also by fungus. The fungus attack did not, however, prepare the way for the insect attack, but succeeded it.

<sup>13</sup> *Dept. Agric. F.M.S. Bull.*, No. 23, p. 27.

<sup>14</sup> *Archief*, 1919, **3**, 43, 222, 374.



reasons for supposing that latex is formed in the latex vessels themselves. Lock<sup>1</sup> is of the same opinion that the laticiferous tissue is an organ, not only for the storage, but also for the manufacture of latex. Bobiloff finds the latex vessels of *Hevea* to contain nucleated protoplasm, in which vacuoles occur. He concludes that the latex of *Hevea* may be presumed to be *cell-sap*.<sup>2</sup>

#### FIELD EXPERIMENTATION WITH HEVEA

Probably few agricultural products offer greater difficulties to the attainment of reliable results in field experimentation than does rubber. With agricultural crops such as those mostly grown in the temperate regions, a sufficient size for experimental plots is  $\frac{1}{160}$ th of an acre; the probable error on a plot of such a size or larger is 5 per cent. of the crop;<sup>3</sup> and the crop is harvested on one occasion only during the year. With rubber a very much larger area must be taken in order to obtain a sufficient number of plants per plot; the natural variation in the yields of trees on a given area is large; and the crop is harvested every day or every other day throughout the year, and is noticeably influenced in its magnitude by the skill and habit of the harvester (tapper). The perennial character of the harvest, and the fact that the harvesting is performed by coolies, demand from the experimenter an amount of supervision very much greater than that demanded by crops yielding an annual harvest.

The normal variations between the yields of apparently-similar plots cut out from an area of uniform age and situation is likely to be such that it is quite impermissible to assume, as has hitherto been done in almost all tapping and manual

<sup>1</sup> *Op. cit.*, p. 69.

<sup>2</sup> Bobiloff Sr. points out that the acid reaction, which he found in latex immediately on its issue from the tree (cf. p. 49), has a bearing on the question of the physiological significance of latex. He draws attention to the following remark of Molisch (*Studien über den Milchsafte und Schleimsafte der Pflanzen*, 1901, p. 43): "Wäre aber der Milchsafte im engeren Sinne, wie ich auf Grund meiner Erfahrungen annehmen muss, Zellsafte, dann würde eine saure oder neutrale oder höchstens eine amphotere Reaction zu erwarten sein."

Further, in a table concerning the latex of different plants (mostly European) investigated by Molisch, in thirty-eight cases the latex was acid and only in four cases amphoteric. Molisch remarks: "Aus dieser Tabelle geht hervor, dass die untersuchten Milchsäfte gewöhnlich sauer, selten amphoter und *niemals* alkalisch reagieren, ein Ergebniss, welches nicht zu Gunsten der Ansicht spricht, dass der ganze Milchsafte als eine Art leicht flüssigen Plasmas zu betrachten sei."

<sup>3</sup> Wood and Stratton, "The Interpretation of Experimental Results," *Jour. Agric. Sci.*, 1909, 3, Pt. 4.

experiments, that such plots will have the same yielding capability, and, hence, that differences which they may display when subjected to different tapping or manurial conditions are due to difference in those conditions, and afford a true comparison of their effect on the yield.<sup>1</sup> Attention was directed to the vitiating effect of natural variation in the plots on the results of most of the published tapping and manurial experiments some years ago.<sup>2</sup> But the conditions which must be observed in order to secure reliable results in field experimentation with *Hevea* have been made the subject of exact statistical treatment only more recently. Papers by Bishop, Grantham and Knapp,<sup>3</sup> by Maas<sup>4</sup> and by Grantham and Knapp<sup>5</sup> demand the study of all who propose to undertake field experimentation with *Hevea*.

From the statistical treatment of the results obtained in ten to twelve months' tapping<sup>6</sup> from plots marked out on areas carefully selected so as to show the greatest possible uniformity of conditions, the extent of the probable error in such plots and the conditions for reliable results were determined. Grantham and Knapp<sup>7</sup> concluded that the optimum size of plot was one hundred trees (say, one acre); the probable error in the yield over a period of six months on such a plot being, when expressed in terms of the mean yield, 6 per cent. Owing to the influence of variations in the site, no substantial reduction in the probable error was to be obtained by increasing the size of the plot; and practical certainty (taken for such agricultural experiments as chances of 30 to 1, corresponding to 3.8 times the probable error) in the recognition of comparatively small differences between the results of different experimental treatments (say, different tapping or manuring conditions), was to be obtained only by duplication of the plots. With one hundred-tree plots the duplications necessary to give practical certainty in the detection of a difference of 6 per cent. was fifteen, of 7 per cent. twelve and of 10 per cent. six. Owing to the difficulty of selecting

<sup>1</sup> For an example of such variations, see Whitby, *Ann. Bot.*, 1919, 31, 318.

<sup>2</sup> Barrowcliff, "The Planning of Manurial Experiments," *Rep. Batavia*, 1914, 132; Whitby, *Plantation Problems of the Next Decade*, 1914, p. 7.

<sup>3</sup> *Archief*, 1917, 1, 335.

<sup>4</sup> *Ibid.*, 1918, 2, 614.

<sup>5</sup> *Ibid.*, 1918, 2, 561.

<sup>6</sup> The tappers were circulated round the plots in a regular way, so as to neutralize as far as possible the personal equation introduced by the tapper's skill, etc.

<sup>7</sup> The present author can testify from inspection as to the great uniformity in appearance and situation of the areas of rubber to which the data of these authors refer.

678.2

1506

N201

a large area of a sufficiently uniform character, it is not usually desirable to exceed ten to fifteen duplications. The conditions for reliable experimentation indicated by Maas's data were somewhat less exacting. Maas concluded that the plots should not be smaller than one hundred trees (he concluded that the most practical size was a tapper's task); that the standard deviation ( $1/0.67$  times the probable error) in three to six months' tapping of such plots was *ca.* 5 per cent.; and that four duplications would suffice to recognize differences of 10 per cent. with certainty.

## CHAPTER II

### LATEX AND ITS COAGULATION

#### PHYSICAL CHARACTERS OF LATEX

THE milk or latex of *Hevea brasiliensis* is a white<sup>1</sup> fluid of a consistency similar to that of thick cow's-milk cream. It is seen, under the microscope, to consist of particles suspended in a serum and engaged in active Brownian movements. Henri gives, as the diameter of the globules,  $0.5-2\ \mu$ ; about half the particles having the latter diameter, and most of the remainder the former. Henri gives, as the number of globules microscopically visible in one cubic mm. of a sample of latex containing 8.7 per cent. of total solids, 50,000. Henri found that, while most of the globules were spherical, some were ovoid. Beadle and Stevens<sup>2</sup> in observations on fresh latex found all the globules to be spherical. More recently Bobiloff<sup>3</sup> has examined the microscopic appearance of the globules in fresh latex derived from different parts of the tree and from different trees. He concludes that latex derived from the bark usually contains four kinds of globules, namely: (a) very small round globules, less than  $0.5\ \mu$  in diameter, (b) round globules from  $1-2\ \mu$  in diameter, (c) pear-shaped globules,  $1.5-2\ \mu$  wide, (d) pear-shaped globules,  $1.5-3\ \mu$  in diameter, having a "tail." He found that in the latex from some trees globules of the two latter kinds were missing. Further: the latex in the leaves, in the branches, in new shoots and in the very youngest roots contained only very small round globules. Bobiloff concluded from his examination of the character of the globules in the latex derived from different parts of the tree, that the latex in new shoots is not derived from the bark and is independent of the rest of the tree (cf. p. 27).

With the object of studying the Brownian movement in latex,

<sup>1</sup> The latex derived from the first tapplings of a tree, before wound response has been established, is often bright yellow; and a few trees here and there persistently give latex of a straw or cream colour (Whitby, *Ann. Bot.*, 1919, 31, 321); but the normal colour of latex obtained under regular tapping is white.

<sup>2</sup> *Koll. Zeit.*, 1913, 13, 207.

<sup>3</sup> *Archief*, 1919, 3, 374.

Henri<sup>1</sup> has made micro-cinematographs of latex. The latex was diluted so that there were about twenty globules in the field of observation at one time; it was magnified to about 600 diameters, and the number of photographs taken per second was twenty. The mean displacement of the globules in one-twentieth of a second was found to be  $0.62 \mu$ . By the addition of N/10 alkali, the mean displacement was reduced to  $0.31 \mu$ , and, by the addition of a small amount of acid (N/32 HCl) short of the amount necessary to produce a clot, to  $0.07 \mu$ . It was found that the Brownian movement could be arrested, without coagulation of any kind occurring, by the addition of 20 per cent. sodium chloride solution in an amount not less than 500 times the volume of the latex. Freudlich<sup>2</sup> has thrown doubt upon this last observation; but Beadle and Stevens<sup>3</sup> have also found that the Brownian movement can be arrested without any aggregation or coagulation occurring. They found that such an arrest could be brought about by adding a suitable amount of acetic acid.

The particles are negatively charged. Henri found in a U-tube cataphoresis experiment with dialysed latex that the globules were displaced towards the anode. After four to five hours the liquid in the vicinity of the cathode had become clear, while the latex in the vicinity of the anode had thickened. Clingett<sup>4</sup> has described the practical application of this behaviour to the separation of rubber from latex on a commercial scale.<sup>5</sup> The latex is contained in a long tank. The electrodes consist of carbon rods contained in porous pots. It would appear that the rubber at first "creams" (see later) around the anodes; and that at this stage reversing the current results in the transference of the rubber to the other pole. If, however, the current is not reversed, following the first stage of creaming, there occurs an increasing degree of coalescence, and finally the formation of a solid layer of rubber on the anode. If the latex is a diluted sample, the whole of the rubber may not, according to Clingett, separate round the anode; but what remains distributed through the latex will, on allowing the latex to stand for a short time, separate, leaving a clear serum. Clingett states that when latex which has been electrically treated is mixed with untreated latex, the latter will

<sup>1</sup> *Le Caoutchouc*, 1906, 106; 1908, 2405; *C.R.*, 1907, 144, 431; *Lects. on Rubber*, 1908, 203.

<sup>2</sup> *Kapillar Chemie*, pp. 328, 346.

<sup>3</sup> *Internat. Cong. Appd. Chem.*, 1912, Vb, 29; *Koll. Zeit.*, 1913, 13, 207.

<sup>4</sup> *Rubber Recueil*, 1914, 377.

<sup>5</sup> See also Cockerill, *I.R.J.*, 1909, 37, 331.

coagulate when stirred. This behaviour may be attributable in part to an aggregated condition of the globules in the treated latex (say, to incipient coalescence). Such aggregates would tend to coalesce to flocks or to a single clot on stirring and might attach to themselves globules of the untreated latex.

It is rather a nice point as to whether latex is to be denominated a suspensoid or an emulsoid. It is commonly described as a colloidal emulsion, but it is perhaps more justly designated, according to Twiss,<sup>1</sup> as a colloidal suspension. Hatschek<sup>2</sup> defines an emulsion as "a disperse system both phases of which, *when considered in bulk and at ordinary temperature*, are liquid."<sup>3</sup> Now, although the nature of the disperse phase of latex is not finally established, and has been supposed by Weber and others to be that of a liquid hydrocarbon from which the solid caoutchouc arises by polymerization, the balance of opinion is very clearly in favour of the view that the globular phase consists of caoutchouc itself (see later), *i. e.* of a material which "considered in bulk and at ordinary temperature" is a solid. Borrowman<sup>4</sup> found that the viscosity of latex was not proportional to increase in the concentration of the disperse phase, but increased more rapidly than did concentration of the disperse phase. When the relative viscosity of latex at different dilutions was plotted against the percentage of total solids in the latex, the curve was a straight line up to a total-solid-content of 10 per cent., and then curved over towards the viscosity axis. It was concluded from this that in regard to viscosity latex behaved as an emulsion rather than as a suspension; the globules being liquid and not solid. It may be suggested, however, that possibly the character of the relation observed between the viscosity and the concentration of the disperse phase may find an explanation in the ready deformability of caoutchouc. Even on the view that latex is a suspensoid and not an emulsoid, it would seem that the last-mentioned circumstance must modify the behaviour of the suspensoid and cause it in some respects to approximate to the behaviour of an emulsoid.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1919, **38**, 47 T.

<sup>2</sup> *Second (1918) Brit. Assocn. Rep. on Colloid Chem.*, London, 1919, p. 16.

<sup>3</sup> Hatschek adds: "The qualifying clause, although not generally stated in such explicit terms, seems desirable as, on one hand, the distinction between solid and liquid becomes somewhat vague with particles approaching ultra-microscopic dimensions, while, on the other, the same system, *e. g.* rosin in water, may be a suspension at a lower and an emulsion at higher temperature."

<sup>4</sup> *Rubber Industry*, 1911, 243.

*Henri's observations.*—Henri<sup>1</sup> studied the coagulation of a sample of preserved latex, the original solid-content of which was 8.7 per cent., and which had been subjected to dialysis until its conductivity was only slightly greater than the conductivity of the distilled water employed. He formulated the following conclusions: (1) Coagulation by electrolytes is determined by the positive ions of the electrolytes. (2) The salts of monovalent metals are without effect. Alcohol is without effect. (3) Salts of metals such as calcium, magnesium, barium, when present in a concentration not less than N., produce coagulation. (4) Salts of heavy metals, such as manganese, nickel, cobalt, copper, zinc, lead, aluminium, produce agglutination when present in a concentration of 0.05-N. (5) Acids produce a clot at a concentration of ca. 0.5-N., or, in the case of sulphuric acid, at a lower concentration. (6) Acetone clots the latex. (7) In general, a feeble coagulant produces a pulverulent precipitate or flocculence, an energetic coagulant a single clot. (8) The structure of the mesh composing the clot, and, correspondingly, the tensile strength of the dried clot vary very greatly with the nature and concentration of the coagulant. For example,  $P_B \times L_B$  for the clot obtained by weak acetic acid was  $0.175 \times 710$ ; for the clot obtained by trichloroacetic acid,  $0.325 \times 680$ ; for the clot obtained by (trichloroacetic acid + two saline coagulants),  $0.660 \times 650$ .

The results of Henri have been widely quoted and have not infrequently been represented as describing the normal behaviour of *Hevea* latex. The behaviour ascertained by Henri bears, however, very little resemblance to the behaviour of latex in the state and at the concentration in which it is habitually handled in the preparation of rubber on the plantation. In this connection, the following points may be remarked: (a) At the outset—before dialysis—Henri's sample of latex was one which had been very much diluted; its solid-content was 8.7 per cent., its conductivity  $3300 \times 10^{-6}$  (equivalent to a 0.25 per cent. solution of sodium chloride), and its freezing-point depression  $0.22^\circ$ . The solid-content of undiluted latex is from 20 to 45 per cent., and the freezing-point depression from  $0.7$  to  $0.8^\circ$ .<sup>2</sup> (b) The specific gravity of Henri's latex (0.973), when compared with its solid-content, is abnormal. The specific gravity of normal fresh latex containing 8.7 per cent. of solids could not, according to de Vries' measurements,<sup>3</sup> be less than ca. 0.993, even if produced by the dilution, with water, of an original latex with the highest

<sup>1</sup> *Loc. cit.*<sup>2</sup> Arisz, *Archief*, 1918, 2, 347.<sup>3</sup> *Archief*, 1919, 3, 183.

solid-content which is encountered. It may be that the low specific gravity of Henri's latex was due to the circumstance that ammonia had been added as a preservative. (Henri does not state in what way the latex was preserved.) The amount of 0.88 ammonia which would be necessary in order to give the specific gravity observed would, however, be more than 20 per cent. And Henri describes the latex as only "faintly alkaline." (c) The latex was dialysed until its conductivity was practically that of distilled water before observations on its coagulation were made.

*Influence of salt concentration on coagulation.*—Latex which had been preserved with a small amount of ammonia was found by Beadle and Stevens<sup>1</sup> to behave normally towards coagulants after two or three days' dialysis, if examined shortly after dialysis. It would appear that Henri's dialysis was more exhaustive than Beadle and Stevens'. Dekker<sup>2</sup> found that ammonia-preserved latex which had been exhaustively dialysed did not react normally to coagulating agents. He concluded that the crystalloids of latex assist in coagulation. And some work by Barritt<sup>3</sup> has shown that the presence of, and the concentration of salts in latex may, particularly under conditions of dilution of the order of those in Henri's experiments, bear an important relation to the coagulation of latex. Barritt's experiments may be described here.

In each case 0.5 c.cs. of (undiluted) latex was mixed with 50 c.cs. of an aqueous solution containing a salt and an acid. This high degree of dilution makes the conditions more comparable with Henri's than are the ordinary conditions of working on the plantation. The concentration of the salt and of the acid was varied systematically; sixty different combinations of salt concentration and acid concentration being employed with each pair of salts and acids examined. It was found in general: (1) For each concentration of acid the amount of coagulation increased as the concentration of salt was increased; and at a sufficient concentration of salt was complete. (2) For each concentration of salt, the amount of coagulation, which was at first complete, diminished as the amount of acid increased, but, in the case of hydrochloric acid and in the case of sulphuric acid, increased as the amount of acid was still further increased, and, finally, became complete again. (3) The width of the gap over which coagulation

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Meded. Delft*, 1916, 529; *Delft Communics.*, 25.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1914, 33, 289.



was incomplete was greater, the lower the concentration of salt; and, at a sufficiently high concentration of salt (different in different cases), coagulation was complete at all concentrations of acid from 0.002-N. to 0.5-N. Plotting the concentration of salt (ordinates) against the concentration of acid at which complete coagulation just occurred (abscissæ), the curve rose to a maximum, and in the case of hydrochloric acid and of sulphuric acid bent over towards the horizontal axis. At all points outside the curve coagulation was complete. (4) In the cases of hydrochloric and sulphuric acids, coagulation occurred at an acid concentration of 0.5-N. without the addition of salt at all. In the cases of acetic, lactic and phosphoric acids, no coagulation occurred at any concentration in the absence of salt. The smallest amount of salt required to produce complete coagulation at all concentrations of acid was in the case of the pair, sulphuric acid—sodium sulphate. At concentrations of sodium salts above 0.04-N., sulphuric acid produced coagulation at all concentrations from 0.002-N. to 0.5-N. (5) The order of effectiveness of metallic ions was Na, K,  $\text{NH}_4$ , Al, Mg—in agreement with Hofmeister's series.

Continuing to comment on Henri's experiments: (d) As examples of differences between the effect of coagulants on Henri's latex and on fresh latex, the following may be mentioned:—

Salts of monovalent metals are not without effect on fresh latex of a rubber-content such as that usually encountered in plantation factories. The author found sodium chloride to produce some coagulation.<sup>1</sup> In the case of such latex, salts of calcium, magnesium and barium produce coagulation at a much lower concentration than that (N./1) mentioned by Henri. The author found, *e. g.*, that 3 c.cs. of a 10 per cent. solution of magnesium sulphate added to 100 c.cs. of a latex containing 12.4 per cent. of rubber had produced clean coagulation when the latex was examined after four hours. The concentration of salt in this case was 0.05-N. The coagulum constituted a single clot: the case was not, as with Henri's latex, a case of agglutination or flocculence only. A similar result was obtained with calcium

<sup>1</sup> When 10 c.cs. of a 10 per cent. solution of sodium chloride was added to 100 c.cs. of latex, containing *ca.* 14 per cent. of rubber, it was found, on examination two-and-a-half hours later, that the latex was set, but that a clean separation into clot and serum had not occurred—the clot had not risen to the top. Even when 50 c.cs. of the solution was used, the coagulation was not complete; the weight of rubber forming the clot being found on the following morning to be 13.5 g., and the weight of the uncoagulated rubber remaining suspended in the serum being 0.7 g.

chloride.<sup>1</sup> In the case of acids, the concentration required to produce coagulation in fresh latex is much smaller than that (0.5-N.) found in Henri's experiments, being, for latex of similar rubber-content to that mentioned above, about 0.01-N. (see later).<sup>2</sup>

#### GENERAL PHYSICAL CHARACTER OF COAGULATION

The latex of *Hevea brasiliensis* is a fluid of such marked instability that its normal behaviour can be studied only in samples which have freshly issued from the tree. The behaviour of preserved latex, such as has been employed for the study of coagulation in Europe, is in many respects different from the behaviour of fresh latex, and may be misleading.<sup>3</sup> This is particularly the case, as Beadle and Stevens show,<sup>4</sup> when the preservative used is formaldehyde; much less so when it is ammonia.<sup>5</sup> Beadle and Stevens point out that the preservation of latex to which formaldehyde has been added is more apparent than real. Microscopic examination reveals the fact that in such latex the globules are no longer separate but have clumped together, forming larger or smaller aggregates. The number of free globules in normal Brownian movement is relatively small or even zero. Often when allowed to stand, and always when diluted and then allowed to stand, such latex creams. The cream can be made to amalgamate to a solid clot by gentle pressure

<sup>1</sup> Whitby, *Internat. Cong. Appl. Chem.*, 1912, 25, 597; *Koll. Zeit.*, 1913, 12, 154.

<sup>2</sup> It is, however, of interest to note that the concentration of acid required (a) in Henri's experiments with dialysed preserved latex, (b) in Barritt's experiments with fresh, diluted latex, and (c) on the far side of the "gap" in experiments (Whitby, p. 47) on the addition of hydrochloric acid and of nitric acid to fresh, 10 per cent. latex is in each case approximately 0.5-N.

<sup>3</sup> This had already been stated with emphasis by Ditmar in 1912. Ditmar wrote (*Koll. Zeit.*, 1912, 10, 239): "Schon geringfügige Zusätze verändern das Gleichgewicht der Emulsion (latex). Es ist daher klar, dass man solche Studien nicht an pasteurisierten oder alten Milchsäften ausführen darf. Schon durch längeres Stehen verändert sich das Gleichgewicht der Emulsion; alle Resultate der Untersuchungen an einer alten Milch entsprechen nicht den Verhältnissen in der Natur und in der Praxis, sind daher nicht wissenschaftlich einwandfrei, daher wertlos. . . . Hierin liegt auch der Grund der so zahlreichen Kontroversen zwischen den einzelnen Forschern. Der eine untersucht in Afrika die frisch von Bäumen fließende Milch, der andere die pasteurisierte, der dritte die drei Monate alte Milch. Keinem steht das gleiche Material zur Verfügung, jedes hat kolloid-chemische Veränderungen erlitten, fast jeder vergisst die Unstabilität kolloider Lösungen."

<sup>4</sup> *Loc. cit.*

<sup>5</sup> Vernet (*Le Caoutchouc*, 1919, 16, 9838) remarks that, even when ammonia is used as the preservative, the coagulability of preserved latex alters gradually.

or even by merely draining off as much as possible of the milky liquor and allowing the product to stand for a few days. Or the "cream" can be separated by filtration, and if then allowed to dry will form a clear sheet of rubber.

The most satisfactory account of the external features of the process of coagulation, as viewed macroscopically and microscopically, is that given by Beadle and Stevens.<sup>1</sup> The present writer's observations on fresh latex are in accord with this account. In the view of Beadle and Stevens, and also of Whitby,<sup>2</sup> the character of the separation of the globules from *Hevea* latex may be conveniently distinguished as falling under one of three heads, namely: creaming, flocculence,<sup>3</sup> coagulation; but there is no fundamental difference between the separations falling under different heads. Beadle and Stevens conclude that the difference between these three types of separation lies solely in the size of the aggregates which the globules form; and that the size is determined by the degree of violence of movement of the free globules brought about by the addition of a coagulating agent or by other means. When, as in the ordinary commercial treatment, an acid is added to latex, there sets in a rapid streaming movement of the globules, which clump together, and are finally seen to be banked up in ridges, forming a connected mass. The result is a network of connected filaments, forming a single clot, such as is usually obtained in the commercial treatment of latex. This type of separation may be termed "coagulation" in the narrower sense of that term.

Under other circumstances—say, with certain weak coagulants or in preserved latex—the translatory movement in the latex is less violent, and isolated aggregates, composed of from perhaps a dozen to several hundred globules, form. The aggregates are not joined up in strings to form a network, but remain separate. This type of separation may be termed "flocculence." Under other circumstances,<sup>4</sup> the aggregates may be smaller, and the globules may separate as a "cream." In Beadle and Stevens' view the production of a coherent coagulum is dependent upon the inducement of violent movements in a sufficient number of

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Probably both creaming and flocculence are included under Henri's term "agglutination."

<sup>4</sup> The author encountered such a circumstance in the treatment of fresh latex with a certain proportion of barium chloride. The addition of 4 c.cs. of a 10 per cent. solution of this salt to latex containing 12.5 per cent. of rubber, caused the latex to separate into a clear serum and a "cream." The latter could be re-distributed through the latex by stirring.

free globules. If a large proportion of the originally-free globules have already become associated with aggregates prior to the addition of a coagulant, there may not be a sufficient number of free globules to lead to clot formation, even with strong coagulants. Hence, it is difficult or impossible to get clot formation with formaldehyde-preserved latex, because such latex consists mostly of aggregates, and it is difficult to get clot formation in a weak, residual latex such as that obtained when the coagulation in a normal latex which has been kept over-night (say, with too little acetic acid) is not quite complete. The present writer has confirmed the presence of microscopic aggregates in such "non-coagulable" latex.

Campbell,<sup>1</sup> in considering the influence of dilution on the rate of coagulation, takes a similar view to that just mentioned. Speaking of the slow rate of coagulation of diluted latex as compared with undiluted latex, he says: "It is not due principally to a slower rate of destruction of the emulsoid state [of the protective agent], for after fifteen minutes the [diluted] latex [to which acetic acid had been added] had changed entirely in character: the solid particles of rubber had formed, but in the form of very small flakes, which took a very considerable time to cohere. Microscopic examination showed that Brownian movement of the globules had ceased. The apparent differences in the rates of coagulation must depend on the rates at which the particles of rubber cohere together to form a coagulum."

According to Beadle and Stevens, in the coagulation of *Hevea* latex the edges of the aggregates remain irregular, whereas in the coagulation of *Castilloa* or *Rambong* latex the edges of the aggregates are smooth; the fusion of the globules in the latter cases being like the union of drops of oil, and in the former case "more like the squeezing together of semi-plastic particles." In the view of Henri,<sup>2</sup> and in that of Schidrowitz,<sup>3</sup> the globules which were present in the latex remain intact in the coagulum. The latter author states that the globules can be recognized in dry, raw rubber when suitable preparations of the latter are examined under the microscope.<sup>4</sup>

<sup>1</sup> *Dept. Agric. Ceylon Bull.*, No. 32, 1917, p. 2.

<sup>2</sup> *Loc. cit.* <sup>3</sup> *J. Soc. Chem. Ind.*, 1909, 28, 6.

<sup>4</sup> It may be mentioned here (although it does not necessarily invalidate Schidrowitz's observations) that it is not impossible for rubber to be deposited from benzene solution in such a way as to form rather definite patterns. It was repeatedly noticed that when a thin layer of a solution of rubber in benzene was evaporated (say, in a Petri dish) in a tropical temperature, the rubber almost invariably showed a tendency to separate out in a pattern.

*Microscopic character of the clot and its vulcanizing properties.*—As already mentioned, it was found in Henri's experiments that the macroscopic structure of the clot varied very considerably with the nature of the coagulant used. Spence<sup>1</sup> demonstrated from the examination under the microscope of suitably stained sections that the protein of raw Fine Hard Para was distributed through the rubber in a way which formed "a peculiar thread-like or fibrous structure." It has sometimes been suggested that the character of the mesh produced under different conditions of coagulation must have an important bearing on the quality of rubber. There is, however, no evidence that such is the case, if the term quality is taken as implying *vulcanizing* quality. Doubtless the structure of the mesh influences the tensile strength of the raw rubber; but, as is pointed out in Part II, it does not appear that the tensile strength of raw rubber bears any close relationship to vulcanizing quality. So far as can be said at present, other conditions being similar, the size of the aggregates in which the rubber separates has no influence on vulcanizing quality. There is no evidence that rubber which has been separated as a cream or as floccules will, on account of the mode of its separation, be inferior to rubber which has been separated as a single, firm clot. Beadle and Stevens<sup>2</sup> state that, when a sample of rubber representing a firm coagulum was compared with a sample representing a loose collection of aggregates (produced by very slow coagulation) which had been filtered or pressed between cloth in order to unite the floccules, no difference in vulcanizing properties could be traced to the firmness or looseness of the coagulum.

Our knowledge of the intimate nature of coagulation is not very extensive or satisfactory. Discussion on the question may be said to date from the observations made by C. O. Weber on *Castilloa* latex in 1903.<sup>3</sup> Weber concluded that the substance of the latex globules was not caoutchouc as we know it, but an oily hydrocarbon (possibly a diterpene), the precursor of caoutchouc, from which caoutchouc was formed by polymerisation during the process of coagulation. Further: in Weber's view the globules were surrounded by a protein envelope; and coagulation was essentially a coagulation of the protein present in the latex, the caoutchouc globules being carried down mechanically. In Weber's conception three ideas may be distinguished, namely:

<sup>1</sup> *Jour. Inst. Comml. Res. in the Tropics*, Liverpool, 1907, 47.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Ber.*, 1903, 36, 3108.

(1) the non-pre-existence of caoutchouc in the latex, (2) the presence of a protein envelope round the globules, and, more generally, (3) dependence of coagulation on protein precipitation.<sup>1</sup> The first of these ideas has never met with much acceptance.

*The question of the pre-existence of caoutchouc in latex.*—It does not appear, however, that certain of the features of Weber's observations have ever been disposed of completely. A repetition and extension of the observations would not be superfluous. Weber states that on shaking fresh *Castilloa* latex with ether, there was within a few seconds a separation into a clear aqueous liquid and an ethereal solution, the latter being perfectly limpid, readily filterable, and containing in one case as much as 43 per cent. of an oily hydrocarbon which easily changed by polymerization into a solid mass of caoutchouc, insoluble in ether. By addition to the ethereal solution of a few drops of hydrochloric acid-containing ether, polymerization to a sponge-like mass rapidly occurred. De Jong and de Haas,<sup>2</sup> also working with fresh *Castilloa* latex, obtained, on extracting latex in excess for twenty-four hours with ether, solutions which were not filterable and which contained only 7.9 and 8.2 per cent. of material, which, they found, was rubber and not an oily hydrocarbon. They found that *Castilloa* rubber itself was not, as Weber had supposed, insoluble in ether.<sup>3</sup> From it they obtained ethereal solutions similar in strength to those which they obtained from the latex. They concluded that the "oily residue" obtained by Weber from his ethereal solution must have contained a large amount of ether. Tschirch<sup>4</sup> accepts this explanation. In a reply<sup>5</sup> to the paper of de Jong and de Haas, Weber maintains his view, and states his conviction that these authors were not dealing with the latex of a genuine specimen of *Castilloa elastica*. It would, however, seem to be unnecessary to assume that the explanation of the conflicting results in question is to be sought in the employment of latex from different species. For it appears that the composition of the rubber (and, presumably, of the latex) from *Castilloa* trees varies greatly. Analyses of *Castilloa* rubber made at the Imperial Institute<sup>6</sup> show different samples, all prepared by

<sup>1</sup> (3) had earlier been suggested by Biffen (*Ann. Bot.*, 1898, 12, 188), and, indeed, by Faraday (*Quart. J. Sc.*, 1826, 21, 19).

<sup>2</sup> *Ber.*, 1904, 37, 3298.

<sup>3</sup> The solvent effect of ether on rubber had earlier been remarked by Payen (*C. R.*, 1852, 34, 5). Cf. Sievers, *J. Amer. Chem. Soc.*, 1917, 39, 725.

<sup>4</sup> *Die Harze und die Harzbehälter*, Leipzig, 1906, Vol. I, p. 990.

<sup>5</sup> *Gummi-Ztg.*, 1904, 18, 101.

<sup>6</sup> Vide H. Brown, *Rubber*, London, 1914, p. 226.

creaming, to range in resin-content from 5.4 to 51.9 per cent. It is not impossible that the explanation of Weber's results may lie in the circumstance that the *Castilloa* latex employed by him was a highly resinous one. Harries<sup>1</sup> obtained by the evaporation of the ethereal extract of fresh latices of *Ficus magnolioides* Borci and of *Ficus elastica* syrupy residues which he separated into an oxygen-containing body,  $(C_{10}H_{16}O)_3$ , and an elastic mass, similar in all its properties to caoutchouc except that it was at first soluble in ether.

Attempts have been made to resolve the question as to the pre-existence of caoutchouc in latex by treating the latex with a rubber solvent and determining the molecular weight of the material dissolved or the viscosity of the solution. Hinrichsen and Kindscher<sup>2</sup> shook a sample of Kickxia (*Funtumia elastica*) latex with benzene, and determined the freezing-point of the benzene solution. After making allowance for the resin in the solution, they arrived at 3173 as the minimum value for the molecular weight of the caoutchouc in the solution, and, as they assumed, of the material composing the globules in the latex. Van Heurn<sup>3</sup> prepared benzene solutions by treatment of *Hevea* latex, and found the viscosity of such solutions to be not less, but, rather, greater than the viscosity of solutions of rubber prepared from the same latex by coagulation with acetic acid. Van Heurn states that the effect of the benzene on the latex was not to produce coagulation. He supposes the solvent to dissolve the globules as such, and concludes that the result of the viscosity measurements is to prove that the globules consist of caoutchouc as present in the coagulated product.

It would not appear, however, that the treatment of latex with the ordinary rubber solvents offers a suitable method of attacking the question of the pre-existence of caoutchouc in the latex. The present author, working with fresh *Hevea* latex, found that the ordinary rubber solvents (benzene, chloroform, carbon disulphide<sup>4</sup>) produced coagulation. And, to judge by the photographs and descriptions in van Heurn's paper, it is not clear that the effect of benzene in van Heurn's work was not to produce coagulation as broadly understood. It may be noted here that Beadle and Stevens state definitely that ether coagulates *Castilloa* latex (cf. Weber's observations).

<sup>1</sup> Ber., 1909, 42, 4329.

<sup>2</sup> Ber., 1909, 42, 4329.

<sup>3</sup> Meded. Delft, 1916, 446; Delft Communics., p. 13.

<sup>4</sup> Ether was not available. Its employment in the tropics is difficult and may be dangerous.

A recent observation which goes to support the generally accepted view that caoutchouc exists as such in the latex prior to coagulation may be noted. De Vries<sup>1</sup> calculates, from determinations of the specific gravity of a large number of samples of latex and of the serum obtained from them after coagulation, that the specific gravity of the globules in the latex of *Hevea brasiliensis* is 0.915. This figure agrees closely with determinations of the specific gravity of purified rubber, and indicates the conclusion that the globules actually consist of caoutchouc; for, did they consist of a material of simpler chemical constitution than caoutchouc, from which caoutchouc was derived by polymerization, it would be expected that their specific gravity would be lower than the specific gravity of their polymer.

As regards the second idea involved in Weber's conception, viz. the occurrence of a protein sheath around the globules: Weber based his view on the appearance of the latex under the microscope. But no subsequent observer has taken Weber's view.

*The protein and coagulation.*—On the question as to how far the coagulation of latex is dependent upon the coagulation of the protein of the latex there has been considerable division of opinion. De Jong and de Haas,<sup>2</sup> combating Weber's view, stated that washed rubber obtained by the coagulation of *Castilloa* latex by means of alcohol contained no nitrogen, and hence no protein; and that by creaming *Castilloa* latex, by repeatedly washing the cream, and, finally, by diluting the cream with water, a latex was obtainable, which, although free from protein, was immediately coagulable by methyl alcohol, ethyl alcohol, acetone, acetic acid or boiling. In these experiments the absence of protein was decided by failure to give the Lassaigne test for nitrogen. Tschirch,<sup>3</sup> however, states that failure to give this test is not conclusive as to the absence of nitrogenous substances in such plant products. Seventeen samples of *Castilloa* rubber analyzed at the Imperial Institute<sup>4</sup> all show the presence of nitrogen; the amount present, calculated as protein, ranging from 0.4 to 3.8 per cent.

Spence found that more than half the protein in the latex of *Hevea brasiliensis*,<sup>5</sup> and in the latex of *Funtumia elastica*,<sup>6</sup> could

<sup>1</sup> *Archief*, 1919, 3, 183.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Op. cit.*, p. 891; Tschirch and Stevens, *Pharm. Centr. H.*; 1905, 46, 501.

<sup>4</sup> *Vide* H. Brown, *Op. cit.*, p. 226.

<sup>5</sup> *Lects. on Rubber*, 1908, 195.

<sup>6</sup> *Quart. Jour. Inst. Comml. Res. in Tropics*, Liverpool, Reprints, 1907.



be removed by means of digestion with trypsin without coagulation ensuing; and hence he rejected the view that the coagulation of latex was dependent upon the removal of a protein envelope from the globules.

An observation with *Castilloa* latex recorded by Biffen<sup>1</sup> would appear in some respects to be opposed to de Jong and de Haas' observation as to the coagulability of creamed latex. Biffen states that the cream obtained by centrifugating *Castilloa* latex, when washed and again shaken up with water, could not be coagulated, as could the original latex, by the addition of alkalis. In another communication de Jong and de Haas<sup>2</sup> record observations which would appear to be in some respects opposed to their view as to the unimportance of the proteins in regard to the coagulation process. They state that the cream obtained from *Castilloa* latex behaved differently towards coagulants (particularly alcohol) from the original latex, and that there was in the serum (which could be separated from the fresh latex by filtration) a nitrogenous substance which exercised a protective action on the rubber globules. When the serum itself or the nitrogenous substance which could be obtained from the serum by precipitation with alcohol was added to the cream, the latter was noticeably protected against the coagulating effect of alcohol or acetone.

Fickendy<sup>3</sup> concluded that in the case of *Funtumia* latex a peptone, not a protein, acted as a protective colloid. He states, also, that the cream from *Castilloa* latex can be stabilized by means of egg-white. Vernet<sup>4</sup> accepts the view that the coagulation of latex by the addition of reagents is due to protein precipitation. Henri and others who have rejected the view that latex coagulation is dependent upon protein coagulation have been content to regard coagulation as sufficiently explained by the neutralization of the negative charges on the caoutchouc globules.

Workers engaged in recent years with fresh latex in the tropics have not shown any inclination to lay down a comprehensive theory which would view the coagulation of latex by various agencies as referable to a single cause—probably because their experience with latex has produced the feeling that the means by which the separation of rubber from latex are so various that, at all events in our present state of knowledge, it is not possible

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Koll. Zeit.*, 1911, 8, 43.

<sup>3</sup> *Ber.*, 1904, 37, 3301.

<sup>4</sup> *Le Caoutchouc*, 1919, 16, 9935.

to bring them within a single, comprehensive view.<sup>1</sup> And no attempt to formulate such a view will be made in the present place. The following points relevant to the issue may, however, be noted:—

(a) It is possible—thus validating, to some extent at least, Weber's conception—for rubber globules to be carried down mechanically in the mesh-work derived from the coagulation of another material. Vernet<sup>2</sup> found that when *Hevea* latex was mixed with two-thirds of its volume of cow's milk, and the mixture was treated with rennin, a coagulum containing the rubber was formed; although rennin had no action on latex alone. Beadle and Stevens<sup>3</sup> found that when a mixture of four-fifths *Rambong* latex and one-fifth *Hevea* latex was treated with acetic acid perfectly clean coagulation followed, although acetic acid had no action on *Rambong* latex alone.

(b) Rubber may be separated from latex by methods that involve the precipitation or association of the protein with the caoutchouc, in a way that does not give a firm, coherent coagulum. The rubber was found to separate in a non-coherent form when such typical protein precipitants as tannic acid and phosphotungstic acid were added to latex.<sup>4</sup> It was found that tannic acid, when employed in amount sufficient to throw down all the precipitable protein (in the case of the usual acetic acid coagulation precipitable protein remains in the serum), gave a clot which could be picked to pieces with the fingers. The separation of the clot by tannic acid was distinguished from ordinary coagulation with acid by being immediate. When tannic acid was employed in an amount smaller than that sufficient to throw down all the precipitable protein, the result might be the separation of the rubber as a kind of slime. The slime, the consistency of which may be judged from the fact that a glass rod could be run through it, became converted into a coherent clot when warmed or in some cases when left over-night. In the latter cases it would appear that bacterial changes in the latex had led to coherency. Beadle and Stevens<sup>5</sup> found that the rubber which had separated as a cream from formalin-preserved latex, when filtered off and dried, contained a normal proportion of protein.

<sup>1</sup> Cf. the remark of Schidrowitz (*Rubber Recueil*, 1914, p. 336). "The more we study the various factors which produce coagulation, the more we are forced to the conclusion that we are dealing with a complex problem which in every case should be decided on its merits."

<sup>2</sup> *Le Caoutchouc*, 1919, 16, 9935.

<sup>4</sup> Whitby, *Agric. Bull. F.M.S.*, 1918, 6, 374.

<sup>3</sup> *Loc. cit.*

<sup>5</sup> *Loc. cit.*

(c) According to Vernet,<sup>1</sup> on rapidly desiccating, by means of a current of air, a thin layer of *Hevea* latex, the globules fuse together but the protein remains largely uncoagulated, since it remains largely soluble. Thus: a sample of latex gave 38.87 per cent. of rubber prepared in the ordinary way and 40.12 per cent. prepared by desiccation as described; but the latter rubber on being washed on the mills weighed only 36.81 per cent. and contained only 0.06 per cent. of nitrogen as against 0.18 per cent.

(d) In the coagulation of latex by heat there is a definite curdling temperature. This temperature, at which curdling occurs sharply, is dependent upon the degree of dilution and acidity of the latex. Thus, for example, a sample of latex, taken about three hours after tapping and diluted with two volumes of water, could be boiled without coagulation occurring. After such diluted latex had been allowed to stand for six hours, it curdled sharply, when heated, at 66°. If the latex which had been thus allowed to stand was diluted with two, four or eight volumes of water respectively, its curdling temperature was respectively 72°, 79°, 84°.²

*A coagulating enzyme.*—Observations by Barrowcliff and by Whitby have given a new aspect to the question of latex coagulation. The latter³ had advanced the hypothesis that the cause of the natural or spontaneous coagulation of *Hevea* latex (see later) was a specific enzyme contained in the latex; and observations made by the former⁴ have rendered it probable that the same hypothetical enzyme is also responsible for artificial coagulation, by acetic acid, as ordinarily practised on the plantations; the function of the acid being to accelerate the action of the coagulating enzyme. Latex which has been sterilized is no longer coagulable in the usual way with a small proportion of acetic acid, but becomes so if treated with a few drops of fresh, unsterilized latex. Eaton and Grantham⁵ had found that latex which had been subjected to the sterilization procedure adopted by them in the experiments which are discussed in the succeeding section was coagulable by acetic acid. Vernet⁶ also mentions that he found sterilized latex to be coagulable by the ordinary proportion of acetic acid.

Barrowcliff contends that the coagulation of latex resembles closely in many respects the coagulation of cow's milk by rennin.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Whitby, *loc. cit.*

<sup>3</sup> Whitby, *loc. cit.*

<sup>4</sup> Barrowcliff, *J. Soc. Chem. Ind.*, 1918, 37, 48 T.

<sup>5</sup> *Agric. Bull. F.M.S.*, 1915, 4, 426.

<sup>6</sup> *Loc. cit.*

Whitby,<sup>1</sup> whose observations agree with Barrowcliff's as to the non-coagulability of latex which has been subjected to the sterilization procedure adopted by Barrowcliff, has brought forward further considerations which support the view that the effect of small proportions of acid in bringing about the coagulation of fresh latex is due to their accelerating action on a coagulating enzyme present in the latex, and is analogous, in regard to the more external characters of the coagulation, to the coagulation of cow's milk by acid-accelerated rennin, rather than to the coagulation of milk by acid in the absence of rennin. Some of these considerations are as follows: In the coagulation of milk by (acetic or lactic) acids in the absence of rennin, there is, as it were, a critical concentration of acid, below which no coagulation occurs, and at which *immediate* clotting takes place. In the coagulation of latex there is no such critical concentration or immediate coagulation: there is a wide range over which acid concentration can be varied, and there are great differences (say, from a period of three minutes to one of eight hours) in the rapidity with which coagulation may occur. In the case of cow's milk, acid may even exercise an anti-coagulating effect when added in less than the critical amount.<sup>2</sup> In the case of *Hevea* latex amounts of acid less than the amount necessary for rapid coagulation have no such anti-coagulating effect: the only result of diminishing the proportion of acid is to render coagulation slower. There is a close analogy between the effect of acids on latex coagulation and their effect on the coagulation of milk by rennin.<sup>3</sup> Even in the absence of all other considerations, the comparative slowness with which coagulation takes place in ordinary plantation practice would seem to afford a strong presumption that the coagulation of latex under the influence of added acid is not a direct effect of the acid but involves the action of an enzyme. In outward aspects the ordinary rubber coagulum resembles the coherent clot (junket) produced in milk by rennin rather than the floccular clot first produced in milk by souring or the addition of acids.

Whitby found that on adding increasing quantities of hydrochloric<sup>4</sup> or of nitric<sup>5</sup> acid to latex, while at first complete coagu-

<sup>1</sup> *Agric. Bull. F.M.S.*, 1918, 6, 374.

<sup>2</sup> Thus, *e. g.*, it was observed in one case that a sample of cow's milk, which could readily be clotted by the addition of 8 c.cs. N. acetic acid per 100 c.cs. of milk, remained liquid for eight days if treated with only 4 c.cs., whereas an untreated control clotted after two days.

<sup>3</sup> For results relative to milk, *vide* Gerber, *C.R.*, 1908, 147, 1320.

<sup>4</sup> *Koll. Zeit.*, 1913, 12, 147.

<sup>5</sup> *Agric. Bull. F.M.S.*, 1918, 6, 374.

lation occurs, a concentration of acid is reached comparatively soon at which no coagulation occurs, but that on continuing to increase the amount of acid added a further point is reached at which coagulation again begins to occur. There is, as it were, a *gap* over which no coagulation occurs. The position of the gap is approximately the same in the case of each of the two acids mentioned. In the case of nitric acid, 1.5 c.cs. of a 10 per cent. solution produced complete coagulation in 100 c.cs. of latex of rubber-content 12 per cent.; 2 c.cs. acting overnight coagulated only 78.4 per cent. of the rubber; 3 c.cs. produced no coagulation at all. On the other side of the gap: coagulation was nearly complete with 10 c.cs., and perfectly complete with 20 c.cs. Barrowcliff suggests that failure to secure coagulation over the gap is due to paralysis, by the acid, of the hypothetical enzyme. If such is the case, it is to be presumed that on the far side of the gap the occurrence of coagulation is due to the acid acting directly and not through the intermediacy of an enzyme. Latex, in the "gap," containing a proportion of acid which would not coagulate it, was coagulable by the addition of the protein precipitant, tannic acid. Coagulation produced in this way is clearly independent of enzymic action. It is interesting to note that the concentration of acid which is effective in producing coagulation *directly* is of the same order as that found necessary for coagulation in Henri's experiments (cf. p. 34, footnote 2).

Hitherto the evidence brought forward in favour of the view that an enzyme plays a part in the coagulation of *Hevea* latex has been circumstantial. The isolation of enzymes from a fluid such as latex presents some difficulty; and the hypothetical coagulating enzyme has not hitherto been isolated.

It would appear to be not improbable that the enzyme survives in ammonia-preserved latex. Beadle and Stevens<sup>1</sup> found such latex, when examined shortly after dialysis, to react normally to coagulants; the amount of acid required to produce coagulation being substantially the same as that required with fresh latex. It is interesting to note that they found that, when such latex was boiled for three minutes and then cooled, it was no longer coagulable by acetic acid in the manner that the unheated latex was coagulable.<sup>2</sup>

<sup>1</sup> *Loc. cit.*

<sup>2</sup> For a recent view of the intimate character of the action of rennin on milk, cf. Schryver, *Proc. Roy. Soc.*, 1913 *et seq.* In this view the inhibition of clotting is regarded as due to the adsorption of simple molecules by the more complex colloids, and the action of the clotting enzyme as

## NATURAL CHANGES IN LATEX

Under tropical conditions the latex of *Hevea brasiliensis* rapidly undergoes spontaneous or natural changes.

It has usually been stated that immediately on its issue from the tree latex is faintly alkaline or neutral in reaction. According to recent measurements by Bobiloff, Sr.,<sup>1</sup> however, only very few trees give neutral latex: in most cases the latex is acid. Bobiloff records the acidity of 105 samples of latex taken on different occasions from 15 trees. He finds the acidity of these samples to range from an amount per litre requiring 25 to one requiring 248 c.cs. N./10 sodium hydroxide for neutralization. The measurements were made by coagulating 50 c.cs. of latex with 25 c.cs. of alcohol, and titrating the serum. If a sample of latex is allowed to stand its acidity increases.

If a sample of undiluted latex of a normal rubber-content (say, 35 per cent.), obtained by tapping trees in the morning, is allowed to stand in the air, it will be found to have set to a solid mass before night. If it is now allowed to stand further, overnight, putrefaction will be found to have occurred; the surface will be yellow or light yellow-brown, slimy and alkaline; the serum will be acid; and probably the under-surface and lower parts of the sides of the coagulum will appear as lacunose, owing to gas-formation in the coagulum. No darkening of the coagulum will have occurred. The serum will be milky in appearance, and will remain so even if a longer period of standing is allowed. If the latex be diluted with water in the first instance, the rate of the natural changes and their results will be considerably altered, and discoloration of the coagulum may be observed. The natural change of *Hevea* latex was first made the subject of study by Whitby,<sup>2</sup> who concluded that four agencies are concerned in it, namely: (a) a coagulating enzyme, (b) an oxidase, (c) and (d) aerobic and anaerobic bacterial action. The oxidase of latex will be considered in a succeeding section.

---

clearing the surface of the colloid of the adsorbed substances, thus permitting coalescence. The influence of salts in hastening or inhibiting clotting is viewed from the standpoint of their effect in raising or lowering the surface tension of the water.

Important recent work on the stability of emulsions, considered from the point of view of the influence of various materials on the interfacial tension between the continuous phase and the particles of the disperse phase, is that of Clowes, *Jour. Phys. Chem.*, 1916, **20**, 407.

<sup>1</sup> *Archief*, 1919, **3**, 408.

<sup>2</sup> *Internat. Cong. Appd. Chem.*, 1912, **25**, 597; *Koll Zeit.*, 1913, **12**, 147.

*The cause of natural coagulation.*—There has been considerable discussion as to the cause of the natural coagulation of latex. Spence<sup>1</sup> had suggested, as a result of work on preserved latex, that oxidizing enzymes might possibly, by producing acid from the carbohydrate complex of the latex proteins and from bodies in the latex of the nature of polyhydric phenols, be responsible for the natural coagulation of latex. Whitby, working with fresh latex, showed that this surmise did not hold, and that the cause of natural coagulation was distinct from the activity of the oxidase: there was no parallelism, but often, rather, an opposition between oxidase activity and the occurrence of natural coagulation; and, for example, natural coagulation took place as well (or better) in the absence of air as in its presence. He found, further, that the natural development of acid in latex and its spontaneous coagulation did not occur *pari passu*; and he concluded that the natural coagulation of latex was due to the action of a specific coagulating enzyme present in the latex. Later, Eaton and Grantham,<sup>2</sup> as the result of some experiments on the natural coagulation of latex which had been subjected to the sterilizing effect of a brief exposure in an autoclave to temperatures of from 90–150°, concluded that it was unnecessary to assume the presence of a coagulating enzyme in latex in order to explain its natural coagulation. Eaton and Grantham's sterilization experiments have been discussed at some length by Barrowcliff<sup>3</sup> and by Whitby,<sup>4</sup> in whose view they are not inconsistent with the conclusion that the agency responsible for the initial setting of fresh latex is enzymic. In the view of Eaton and Grantham<sup>5</sup> the natural coagulation of latex is due to bacterial action.<sup>6</sup> This view is also taken by Vernet,<sup>7</sup> who states that latex collected under sterile conditions<sup>8</sup> and sealed in a sterile vessel was still liquid after the lapse of one month.

<sup>1</sup> *Lects. on Rubber*, 1908, 198; *I.R.J.*, 1910, **41**, 94. Cf. *J. Soc. Chem. Ind.*, 1918, **37**, 262.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Agric. Bull. F.M.S.*, 1918, **6**, 374.

<sup>5</sup> *Loc. cit.*; see also Eaton, *Agric. Bull. F.M.S.*, 1917, **6**, 156; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 276 *et seq.*

<sup>6</sup> The bacterial flora of *Hevea* latex has been studied by Denier and Vernet, *C.R.*, 1917, **165**, 123.

<sup>7</sup> *Loc. cit.*; *Le Caoutchouc*, 1920, **17**, 10193.

<sup>8</sup> The bark of a tree in tapping was scraped with a knife which was constantly passed through a flame; the surface of the bark was slightly heated and was allowed to cool; a piece of tin-plate, suitably bent to hold latex, was pressed into the bark, and the latex was collected in a sterilized pipette of the kind used for the collection of blood in bacteriological work. The experiments were made in Cochin China.

Campbell,<sup>1</sup> as a result of experiments on the relation to natural coagulation of calcium salts (which are generally recognized as having an accelerating effect on the action of enzymes), accepted the enzymic hypothesis. Whitby<sup>2</sup> had already found that small quantities of calcium chloride were capable of leading to the coagulation of latex. Campbell studied the relation of calcium salts to the coagulation of latex more closely. He found calcium chloride to be effective in bringing about coagulation when present in much smaller quantities than barium chloride; and, further, that, as in the case of the coagulation of blood and of milk, the calcium precipitants, potassium oxalate and sodium fluoride,<sup>3</sup> very noticeably retarded or even inhibited the coagulation of latex. Vernet<sup>4</sup> is of opinion that potassium oxalate and sodium fluoride do not owe their anti-coagulating effect to the fact that they are precipitants of calcium, but simply to their antiseptic action. Barrowcliff,<sup>5</sup> however, states that the addition to latex of a solution of a calcium salt even in as small a quantity as 0.002 per cent. of calcium reduced the time required for the natural coagulation of latex in a closed vessel from ten to six hours, and in a quantity of 0.01 per cent. to about four hours.

Barrowcliff<sup>6</sup> has brought forward observations in support of the enzymic hypothesis of natural coagulation. He found that when latex was sterilized by running it into an equal volume of water maintained at the boiling-point, and was then left, without any addition, to stand in an open vessel, it remained uncoagulated for several days,<sup>7</sup> but if inoculated with a drop of fresh latex underwent coagulation overnight in the same manner as an unsterilized control. He also found that natural coagulation took place normally in latex, contained in a closed vessel, which had been treated with toluene—a substance which is generally recognized as toxic to bacteria but innocuous to enzymes. Natural coagulation was also unaffected by thymol. It was, however, prevented by hydrocyanic acid—a substance which is generally recognized as an enzyme paralyzer. Whitby,<sup>8</sup> in the course of a comparison between latex coagulation and the

<sup>1</sup> *J. Soc. Chem. Ind.*, 1917, **36**, 274.

<sup>2</sup> *Koll. Zeit.*, 1913, **12**, 154.

<sup>3</sup> The present writer had earlier, in some unpublished observations, found ammonium fluoride to act in a similar manner.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Loc. cit.*

<sup>7</sup> It may be remarked that Eaton, similarly, found (*Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 281), that sterilized latex did not, as unsterilized latex does, undergo natural coagulation in twenty-four hours, even when sugars were added to the latex in order to assist fermentation.

<sup>8</sup> *Agric. Bull. F.M.S.*, 1918, **6**, 374.



coagulation of cow's milk, brings forward further considerations in favour of the enzymic hypothesis. From a survey of the subject, Twiss<sup>1</sup> concludes: "The evidence seems so circumstantial as to justify the claim that the initial formation of the coagulum in fresh latex allowed to undergo natural change is due to enzymic action, and that the same agency activated by acids is responsible for the customary coagulation by acetic acid."

Whitby views bacterial action, in relation to the occurrence of natural coagulation in latex, as a secondary factor only. It may be remarked that, if the acidity developed in latex by bacterial action is viewed as having the effect of accelerating the action of the hypothetical coagulating enzyme, a reconciliation of the enzymic and bacterial hypotheses would appear to be possible.

As already remarked, the results of aerobic and of anaerobic bacterial activity in latex which is allowed to undergo natural change can be distinguished. The production of the alkaline-reacting slime, to which reference was made, is the result of aerobic activity, involving decomposition of protein (putrefaction). The amount to which the slime is formed is influenced by the extent of surface which the latex exposes to the air. A shallow layer of latex ( $\frac{1}{4}$ – $\frac{1}{2}$  in. in depth) left for twenty-four hours may consist entirely of yellow, evil-smelling alkaline slime;<sup>2</sup> whereas in the case of a deep mass of latex (say, in a tall, narrow cylinder) left for a similar period the layer of slime will be comparatively shallow; the lower part of the mass consisting of a firm coagulum. As already remarked, latex below the slimy layer, *i. e.* under ordinary circumstances the greater part of the latex, becomes strongly acid as a result of natural change. The development of acidity is to be regarded as due to anaerobic change of, in the first place, the carbohydrate<sup>3</sup> of the latex (fermentation). The change in question is accompanied by the formation of carbon dioxide, which, in the case of undiluted latex, produces bubbles in the coagulum, and, if the latex is contained in a sealed vessel, may make the coagulum spongy throughout.

*Natural coagulation under anaerobic conditions.*—It was shown

<sup>1</sup> *Ann. Repts. Prog. Appd. Chem.*, 1918, **3**, 304.

<sup>2</sup> Eaton, *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 278.

<sup>3</sup> It should be noted that, as mentioned on p. 68, inositol is capable of undergoing lactic acid fermentation. Hence it is not impossible that some of the natural acidity of latex which has been allowed to stand may be due, not to its sugar, but to its quebrachitol.

by Whitby<sup>1</sup> that, whereas in undiluted latex left in the air overnight to undergo spontaneous coagulation, putrefaction always occurred, and the serum was always milky, putrefaction could be avoided, and complete coagulation and a clear serum obtained, if the latex were sealed up in closed vessels, so as to prevent the occurrence of aerobic bacterial activity. The use of this method, of anaerobic natural coagulation, for the preparation of rubber on an industrial scale will be examined in a later chapter.

The strongly-acid serum obtained by anaerobic natural coagulation becomes, when exposed for some time to the air, strongly alkaline and develops typical products of putrefaction.<sup>2</sup>

Eaton and Grantham<sup>3</sup> showed that by adding sugars to latex the fermentative activity could be encouraged and the putrefactive activity discouraged, with a favourable effect on the completeness of the coagulation. The addition of sugar is particularly useful in ensuring the clean and smooth coagulation of latex left to undergo natural coagulation in closed vessels. Eaton and Grantham found that from 0.1–0.2 per cent. of dextrose or other sugars added to latex of a rubber-content of 25–30 per cent. was a suitable quantity. Gorter and Swart<sup>4</sup> recommend somewhat larger quantities. The present author has, however, usually found the proportions mentioned by Eaton and Grantham to be satisfactory. Whilst the sugar-treated latex is standing overnight, the sugar is entirely destroyed. Gorter and Swart found that it became converted chiefly into lactic acid. They also found that acetic acid was formed in an amount less than the amount of the lactic acid, and not more than one-quarter of the whole. They also recognized the presence of a small quantity of succinic acid, produced as a by-product of alcoholic fermentation in the latex. The employment of sugar in the practical application of anaerobic natural coagulation will be considered elsewhere.

The influence of the addition of sugar to latex in preventing putrefaction and in bringing about an increase in the degree of acidity developed is in accord with the principles, concerning bacterial metabolism, established by the work of Kendall and his collaborators.<sup>5</sup> It does not appear to be necessary to assume

<sup>1</sup> *Koll. Zeit.*, 1913, 12, 147.

<sup>2</sup> Whitby, *loc. cit.*

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Meded. v. h. Rubberproefstation West-Java*, 1916, No. 6.

<sup>5</sup> *J. Biol. Chem.*, 1912, 12, 13, 19, 215, 465; 1913, 13, 63; *J. Amer. Chem. Soc.*, 1913, 35, 1201.

The principles in question are enunciated by Kendall as follows: "A most fundamental principle of bacterial metabolism is expressed by stating 'Fermentation takes precedence over putrefaction'; that is to say, bacteria in general, which can utilize both carbohydrate and protein, act upon the

that the effect of adding sugar to latex is to produce conditions favourable to the growth of certain (anaerobic) species of bacteria attacking sugar and forming acid, and unfavourable to the growth of other (aerobic) species leading to putrefaction. The change produced by the addition of sugar in the character of the fuel-supply available to them would appear to suffice to explain the production by the same species of bacteria of putrefaction, with accompanying alkalinity, under one set of circumstances, and of fermentation, with accompanying acidity, under another.<sup>1</sup>

#### THE OXIDIZING ENZYMES OF LATEX

Racibowski,<sup>2</sup> in Java, examined the latex of a considerable number of different plants, including *Manihot glazovii* and various species of *Euphoria*, and in all cases got a strong reaction (peroxidase reaction) with tincture of guiacum or  $\alpha$ -naphthol in the presence of hydrogen peroxide. Weber<sup>3</sup> thought that the darkening of rubber prepared from *Castilloa* latex was probably due to the presence of an oxidizing enzyme in the latex. Spence,<sup>4</sup> by soaking

---

former in preference to the latter when both are present in the same medium. . . . By fermentation is meant 'the action of micro-organisms upon carbohydrates,' and by putrefaction is meant 'the action of micro-organisms upon nitrogenous substances.' " "Whenever bacteria can utilize both carbohydrates and protein for their vegetative activity (for fuel), and both are present in the medium in which these organisms are growing, the carbohydrate is invariably selected in preference to the protein. . . . The products of proteolytic activity, which are only formed when bacteria are utilizing protein for fuel, are alkaline, nitrogenous substances; the products of fermentation, on the contrary, which are formed when bacteria are utilizing carbohydrates for fuel, are non-nitrogenous, acid products."

The "sparing" influence of sugars on putrefaction had earlier been studied in less extensive and less systematic experiments than those of Kendall by Hirschler (*Zeit. f. physiol. Chem.*, 1886, **10**, 306) and by Siminitzki ("Beitrag zur Lehre des Einflusses der Kohlenhydrate auf die Eiweissfäulnis," *Zeit. f. physiol. Chem.*, 1903, **39**, 99. The literature to date is given here.) Hirschler notes the following as having a sparing influence on the bacterial decomposition of proteins, namely: cane sugar, glycerol, dextrine, starch, glycogen.

<sup>1</sup> Whitby, *Agric. Bull. F.M.S.*, 1918, **6**, 513; *Le Caoutchouc*, 1919, **16**, 9788.

<sup>2</sup> "Ein Inhaltskörper des Leptoms," *Ber. Deut. bot. Ges.*, 1898, **16**, 52; "Weitere Mittheilungen über das Leptomin," *Ibid.*, 1898, Heft. 5, 22. VI; "Einige Demonstrationsversuche mit Leptomin," *Flora*, 1898, **85**, 362.

<sup>3</sup> *Ber.*, 1903, **36**, 3108. For the recognition of an oxidase in *Castilloa* latex Weber relied upon the blueing of iodide-starch paper. Aso and also Wolff and de Stoecklin (*C.R.*, 1908, **146**, 1415) have, however, pointed out that this reaction, in the case of plant juices, is to be attributed to nitrous acid.

<sup>4</sup> *Biochem. Jour.*, 1908, **3**, 165.

thin slices of the rubber in water, was able to extract an oxidase from Fine Hard Para. The oxidase in question gave the characteristic colour reactions for oxidizing enzymes only after the addition of hydrogen peroxide; and hence was not, in the strict sense of the term, an oxidase, but rather a peroxidase. The oxidase was not a tyrosinase. Further: the extract had the properties of a catalase.

Spence found the latex of *Funtumia elastica* to give a feeble reaction for oxidase in the absence of hydrogen peroxide; and, a little later,<sup>1</sup> found each of four samples of preserved *Hevea* latex examined to give "a marked positive reaction without hydrogen peroxide and a still more intense reaction in the presence of this chemical" when tested by the following oxidase reagents, namely: the "indophenol" mixture of Röhm and Spitzer,<sup>2</sup> an aqueous solution of *p*-phenylenediamine hydrochloride, an aqueous solution of hydroquinone. Spence was able to isolate from the latex a preparation of the oxidase by coagulating the latex with 40 per cent. alcohol, and then precipitating the mother liquor with absolute alcohol. Whitby<sup>3</sup> examined a large number of samples of fresh latex from plantation trees, and in all cases obtained a strong reaction for peroxidase (*i. e.* in the presence of hydrogen peroxide); but in no case obtained a positive reaction for oxidase (*i. e.* in the absence of hydrogen peroxide), even when the latex was tested immediately after it had issued from trees the rubber from which showed an exceptionally strong tendency to darken rapidly, and the latex from which gave, correspondingly, an exceptionally strong reaction for peroxidase.<sup>4</sup> Cayla<sup>5</sup> examined the latex<sup>6</sup> of eighteen different species and found all but four to react with oxidase reagents in the absence of hydrogen peroxide.

<sup>1</sup> *Biochem. Jour.*, 1908, **3**, 351.

<sup>2</sup> *Ber.*, 1895, **28**, 567.

<sup>3</sup> *Koll. Zeit.*, 1913, **12**, 147.

<sup>4</sup> The reagents employed in this examination for the detection of oxidizing enzymes were tincture of guaiacum and pyrogallol. Regarding the former of these reagents: the quantity of 1-volume hydrogen peroxide used was 0.5 c.c. for 1 c.c. of original latex plus 5 c.c. of water. It was found to be impermissible to employ hydrogen peroxide in large quantity, as the reagent was observed, when employed in sufficient quantity, to coagulate latex. When employed in small amount (say, 0.5 c.c. of 30-volume hydrogen peroxide per 100 c.c. of a 10 per cent. latex) its effect, on the contrary, was to prevent or retard coagulation. Spence (*Biochem. Jour.*, 1908, **3**) considers tincture of guaiacum to be an unsuitable reagent for the detection of oxidizing enzymes in latex, owing to the coagulating effect of its alcohol. The present writer, however, found it to reveal the presence of peroxidase satisfactorily in the latex of *Hevea* (and in Jelutong latex). And the negative results obtained with it on latex in the absence of hydrogen peroxide were confirmed by the use of the pyrogallol reagent.

<sup>5</sup> *Soc. de Biologie*, 1908, **45**, 128.

<sup>6</sup> Presumably preserved latex.

The four in question reacted in the presence of hydrogen peroxide. Koketsu,<sup>1</sup> in the case of latices from eleven different plants examined by him by means of guaicum and  $\alpha$ -naphthol, found in all cases a distinct peroxidase reaction, but no reaction, or only an indefinite one, for oxidase.

When, as in the industrial preparation of rubber, the coagulation of *Hevea* latex is brought about by the addition of a small proportion of acetic acid, the action of the oxidase of the latex usually displays itself by producing, when the latex is left overnight, superficial darkening of the upper surface of the coagulum which is exposed to the air; and, later, of the wet rubber into which the coagulum may, by washing and rolling, be converted. The superficial darkening of the wet, unrolled coagulum is usually represented by a purple to dark grey colour. The darkening of the washed and rolled rubber usually has the result of giving the dry rubber a light or darker brown colour. If the action of the oxidase is inhibited, then the dry rubber, in the case of the crêpe form, is of a pale amber colour. If the action of the oxidase is not inhibited, crêpe is usually of a noticeable darker and browner tint, even though the superficial portions of the coagulum which had discoloured in the coagulating vessel were cut away before the coagulum was crêped. Even though the coagulum is thoroughly masticated in a stream of water on a washing mill, some of the oxidase, which Spence<sup>2</sup> showed to be associated with the protein of the coagulum, is retained by the coagulum. It has been a frequent experience that substances present in or added to latex before coagulation are to some extent retained very firmly by the coagulum. It was found, *e. g.*, that stains added to latex were largely taken up by the coagulum and retained during subsequent washing.<sup>3</sup> It is probable that the retention (? adsorption) of the stain is due to the protein of the coagulum.<sup>3</sup>

*Oxidase activity and vulcanizing properties.*—There is no ground for believing that the production of discoloration in rubber as a result of oxidase activity has any influence on the vulcanizing properties of the rubber. But the plantations have from the first found it advisable, on account of the predilections of the markets, to aim at producing, where crêpe rubber is in question, the palest possible product, and, thus, at destroying the oxidizing

<sup>1</sup> *Bot. Mag., Tokyo*, 1913, **27**, 133; *J. Coll. Sc., Tokyo*, 1913–15, **35**, Article 6, p. 57.

<sup>2</sup> *Biochem. Jour.*, 1908, **3**, 165.

<sup>3</sup> Whitby, *loc. cit.*

enzyme or inhibiting its action. The method which for several years past has been universally adopted in this connection has been the treatment of the latex with a small proportion of sodium bisulphite. Formerly, other less successful or less innocuous methods were tried. The use of sodium bisulphite in this connection will be discussed later.

*Influence of reagents on oxidase activity.*—The activity of the oxidase, as indexed by the rate or amount of discoloration occurring in the latex or coagulum, is considerably influenced by the degree of acidity of the medium. It was found<sup>1</sup> that an acid medium was necessary in order that grey oxidation products might arise, but that large amounts of acid diminished or inhibited their production. Although, as already remarked, undiluted latex left to undergo spontaneous change does not show grey discoloration if untreated, it is found to do so if treated with a small proportion of acid (say, 2 c.cs. N. sulphuric acid to 100 c.cs. of latex). The larger the amount of acid employed for the coagulation of the usual diluted latex, the smaller is the tendency to discoloration (and putrefaction) in the coagulum.

A number of substances have been noticed which greatly accelerate the activity of the oxidase. Such are most prominently phenolic bodies—phenol,<sup>2,3</sup> pyrogallol,<sup>2</sup> picric acid,<sup>2</sup> pyroligneous acid,<sup>2,4</sup> amidol.<sup>3</sup> In the fact that phenolic substances are favourable to discoloration in *Hevea* rubber is to be found the explanation of the dark colour of such rubber as Fine Hard Para and smoked sheet.<sup>5</sup> In these cases the wet rubber has been subjected to the action of smoke.

Other substances which have a still more marked accelerating effect on oxidase activity in latex and rubber are silver nitrate and calcium chloride.<sup>6</sup>

#### CHEMICAL COMPOSITION OF LATEX AND RUBBER

The first chemical examination of rubber-yielding latices was made by Fourcroy<sup>7</sup> in 1791. Fourcroy's examination yielded very little knowledge as to the chemical composition of latex,

<sup>1</sup> Whitby, *loc. cit.*

<sup>2</sup> Whitby, *loc. cit.*

<sup>3</sup> Eaton, *Dept. Agric. F.M.S. Bull.*, No. 17, 1912, p. 30.

<sup>4</sup> Eaton and Whitby, *Agric. Bull. F.M.S.*, 1917, 5, 124.

<sup>5</sup> *Rep. Batavia*, 1914, 164; *J. Soc. Chem. Ind.*, 1916, 35, 493.

<sup>6</sup> Whitby, *loc. cit.*

<sup>7</sup> "Sur le suc qui fournit la Gomme élastique," *Ann. chim. phys.*, 1791, 11, 225-36.

but offers one or two points which may be noticed because of their historical interest. The latices examined were derived from *Hevea guianensis* and *Jarropha elastica*. Fourcroy supposed that the absorption of oxygen from the air was the chief cause of the coagulation of the latices. He recognized that acids caused precipitation and that alkalis had a reverse effect; and he recommended that latex should be treated with soda or with potash on withdrawing it from the tree in order to preserve it in a liquid condition, so that it might be shipped to Europe for the manufacture of rubber articles. From the serum he noted the separation of a large quantity of crystals with a sugary taste, which were very soluble in water and could be re-crystallized from alcohol. It is not impossible that he had in hand here one of the derivatives of inositol such as have since been recognized in various latices. Later, Faraday<sup>1</sup> made a fuller and more exact analysis of a sample of latex, and recognized the presence of protein and also of soluble nitrogenous substances. Faraday's results have been repeatedly quoted as representing the chemical composition of the latex of *Hevea brasiliensis*. It is, however, very improbable that the latex in question was from *Hevea brasiliensis*, if only on account of the fact that its specific gravity was 1.0117 (caoutchouc-content, 31.7 per cent.). Beadle and Stevens<sup>2</sup> think that the latex was probably from *Castilloa elastica*. Faraday himself says nothing about the origin of the sample, beyond the remark that "The fluid, I understand, had been obtained from the southern part of Mexico."

*Chemical composition of rubber.*—The composition of the rubber obtained, by the methods of rolling, washing and drying practised on the plantations, from the coagulum given by the latex of *Hevea brasiliensis* is usually stated in terms of moisture (or, sometimes, loss on washing and drying), ash, "resins," "protein" and "caoutchouc." "Resins" represent that portion of the dry rubber which is soluble in acetone. "Protein" is estimated by determining the nitrogen-content of the rubber by means of the method of Kjeldahl and multiplying the result by the conventional factor 6.25. Alternatively "protein" may be determined by ascertaining what amount of the rubber is insoluble in various organic liquids. This amount may be taken as consisting of (protein + ash). In view, however, of the uncertainties connected with the determination of insoluble matter (see later), this method is, at all events in the present

<sup>1</sup> *Quart. Jour. Sc.*, 1826, 21, 19.

<sup>2</sup> *Analyst*, 1911, 36, 6.

state of rubber analysis, probably less satisfactory than the estimation of protein by a Kjeldahl determination. The exact significance of these quantities will form the subject of discussion later. "Caoutchouc" is estimated by difference. Methods for the direct determination of caoutchouc by means of one of its addition compounds have been proposed, but no such method has hitherto found any general acceptance. The tetrabromide, especially, has received attention as possibly lending itself to the direct determination of caoutchouc, and has been the subject of a very large number of papers. In general, the compounds of caoutchouc are not sufficiently well-defined to permit of their employment in an analytical connection.

The following figures may be quoted, as indicating the chemical composition of typical plantation rubber. A collection of samples, in two groups, of plain sheets prepared on different occasions according to the same procedure<sup>1</sup> showed the following results<sup>2</sup> :—

TABLE IX

(Percentages)

GROUP I (TREES SEVEN YEARS OLD.—SEVENTEEN SAMPLES)					
	Loss on Washing.	Ash.	Resin.	Protein.	Caoutchouc.
Mean . . . . .	0.60	0.225	2.81	2.33	94.63
Extreme figures in different samples . . . . .	0.32–1.30	0.15–0.28	2.30–3.47	2.04–2.68	95.36–93.60
GROUP II (TREES SIXTEEN TO TWENTY YEARS OLD.—EIGHT SAMPLES)					
	Loss on Washing.	Ash.	Resin.	Protein.	Caoutchouc.
Mean . . . . .	0.57	0.256	3.00	2.28	94.44
Extreme figures in different samples . . . . .	0.40–0.90	0.23–0.31	2.72–3.46	2.09–2.45	94.96–93.89

Fol<sup>3</sup> records the results of the analyses of 137 samples of plantation rubber. The collection contained 36 samples of sheet (all except one smoked) and 101 samples of crêpe. The

<sup>1</sup> Apparently the latex was diluted to a rubber-content of 15 per cent.; and the amount of acetic acid used for coagulation was 1 part to 1000 parts of diluted latex (*Dept. Agric. Ceylon Bull.*, No. 24, p. 11); but this is not entirely clear.

<sup>2</sup> *Dept. Agric. Ceylon Bull.*, 1916.

<sup>3</sup> *Rep. Batavia*, 1914, p. 179; *Meded. Delft*, 1916, p. 214.



extreme figures found for the individual analytical items were as follows :—

TABLE X  
(Percentages)

Moisture . . .	0.18-1.08	Protein . . .	2.18-3.76
Ash . . .	0.15-0.87	Caoutchouc . . .	94.62-92.13
Resin . . .	1.52-3.81	Degree of acidity <sup>1</sup> .	0.1 - 1.3

The manner in which the analytical quantities for samples of rubber may be influenced by the method of preparation will be considered at various points later.

*Chemical composition of latex.*—It must be confessed that our knowledge of the composition of the latex of *Hevea brasiliensis* is, particularly when its fundamental importance for an understanding of the physiology and for the rational exploitation of latex is borne in mind, at present insufficiently exhaustive. A number of rough analyses, in which ash, "resin," "protein" and (by difference) caoutchouc were determined, were made at various times subsequent to Faraday, but need not be quoted here. More recently some investigations of greater thorough-

<sup>1</sup> "Residual acidity."—The quantity in question here is determined by extraction with water and titration with 0.01-N. alkali. It is expressed here as the No. of c.c.s. of 0.01-N. alkali per gram of rubber.

The original intention in determining this quantity, which has been called "residual acidity," was to ascertain the amount of acetic acid, used for latex coagulation, which had been retained by the dry rubber. It is, however, probable that it does not permit of this: that "residual acidity" does not represent a residuum of acetic acid. (Whitby, "Plantation Problems of the Next Decade," *Weltervreden*, 1914, p. 20-1). Rather is it connected with the retention of water-soluble serum solids by the rubber, and, possibly, with the occurrence of fermentation in the coagulum. In agreement with the view just expressed is the fact that the "degree of acidity" of sheets is higher than that of crêpes—in Fol's collection of samples it is five times as great. And, further, rubber obtained simply by the evaporation of latex, without any addition of acid, shows a figure for "degree of acidity" higher even than that of any of the sheets in this collection, viz., 1.5 (*Delft Communics.*, p. 68). Schidrowitz and Goldsbrough (*I. R. J.*, 1912, 44, 1148), in the examination of samples of sheet prepared by the present writer, found the "residual acidity" to be greater when a smaller amount of acid had been used for coagulation than when a large excess had been used, as the following figures show :—

Relative quantities of acetic acid for equal volumes of latex									
	0.5	2	1	2	3	6	12	24	
Acidity, per cent.	0.055	0.046	0.031	0.026	0.012	0.011	0.010	0.012	

The first two samples formed one series, prepared from a given batch of latex, and the remaining six samples another series, prepared from another batch of latex.

ness into the composition of latex have been made. The following results may be noted:—

Beadle and Stevens<sup>1</sup> found the composition of the total solids obtained by the evaporation of latex to be, in two cases, as follows, when expressed as resin (acetone extract), protein, ash and caoutchouc.

TABLE XI  
(Percentages)

	I. Dried latex from four-year-old trees.	II. Dried latex from ten-year-old trees.	Calculated composition of latex I.	Calculated composition of latex II.
Resin . .	4.06	4.13	1.22	1.65
Protein . .	4.90	5.08	1.47	2.03
Ash . .	0.80	1.75	0.24	0.70
Caoutchouc . .	90.24	89.04	27.07	35.62
Water . .	—	—	70.00	60.00

Latex collected from the base of the leaves had a noticeably different composition, the protein being 13.02 and the resin 7.12. But it is open to question as to whether this latex would not be contaminated with other plant juices. Aqueous extracts of the total solids from the above latices showed the following results for sugars calculated as percentages of dextrose on the rubber.

TABLE XII

	I.	II.	Latex from petioles.
Before inversion . . . .	Trace	None	0.36
After „ . . . .	0.79	0.34	2.25

In the case of three other samples of latex (preserved with formalin) the same authors<sup>2</sup> separated the crystalloid constituents by dialysis, and examined them separately. The following table shows the results of this examination. The results are expressed as percentages on the original latex. The total solids prior to dialysis in the three samples, A, B, C, amounted respectively to approximately 30, 22.0 and 25.8 per cent.

<sup>1</sup> *Analyst*, 1911, 36, 6.

<sup>2</sup> *Internat. Cong. Appd. Chem.*, 1912, 9 17; *Koll. Zeit.*, 1913, 13, 207.

TABLE XIII

Sample.	A	B	C
Total solids in dialysate . . . . .	2.61	1.65	1.52
Sugars after inversion . . . . .	0.24	0.19	0.15
Nitrogen . . . . .	0.048	0.054	0.043
Ash . . . . .	0.41	0.29	0.24
Sulphuric acid (SO <sub>3</sub> ) . . . . .	0.008	0.009	0.008
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> ) . . . . .	0.13	0.09	0.06
Lime (CaO) . . . . .	0.013	0.014	0.004
Magnesia (MgO) . . . . .	0.02	0.019	0.008
Potash (K <sub>2</sub> O) . . . . .	0.19	0.17	0.14

The inorganic constituents estimated separately account for the greater part of the ash; and in sample B the figure for the ash and the total figures for the separate constituents estimated balance almost exactly. Hence, it appears the main dialysable inorganic constituents of the latex are calcium, magnesium and potassium phosphates, the latter predominating. As, however, there is insufficient phosphoric acid to satisfy the potash alone, a great part of the inorganic bases may be in combination with organic acids.

The separate constituents of the total dialysate solids (*i. e.* sugars, ash, and "nitrogen calculated as protein") estimated above account for less than half of the material; the amounts left unaccounted for in the three samples being respectively 1.66, 0.83 and 0.86 per cent. It is probable from other investigations (see later) that these amounts represent in large part quebrachitol. The amount of nitrogen remaining in the latex after dialysis was determined. When it, and also the nitrogen in the dialysate were expressed as protein, the following results were obtained:—

TABLE XIV

(Percentages)

	A	B	C
Non-diffusible . . . . .	1.26	0.87	1.04
Diffusible . . . . .	0.30	0.34	0.27
Total . . . . .	1.56	1.21	1.31
Total expressed as percentage of total solids	5.2	5.5	5.1

Comparing the (similar) figures given in the bottom row with the figures given in Table IX for the protein-content of typical

samples of dry plantation rubber, it will be observed that roughly one-half of the "nitrogen calculated as protein" is in ordinary practice retained by the washed and dried coagulum.

The results of an examination of latex serum are given by Gorter.<sup>1</sup> Two litres of fresh latex was diluted with 0.9 l. of water and coagulated by warming for a short time on the water-bath with 100 c.cs. of 5 per cent. acetic acid solution and then allowed to stand for two hours. The serum was pressed out as completely as possible; the total-solid-content was determined by drying at 105°; the nitrogen-content was determined on 50 c.cs. by the Kjeldahl method. The optical activity was determined; and, from the result, the proportion of quebrachitol was calculated. Gorter justifies the last procedure by stating that two-thirds of the quantity of quebrachitol calculated from the polarimetric reading could be actually crystallized. The very great solubility of quebrachitol in water and the presence of potassium salts prevented its further crystallization. The sample of the latex in question was from 35-year-old trees, and its rubber-content, determined by coagulation by acetic acid, was 37.0 g. per 100 c.cs. The results for the serum, expressed as grams per 100 c.cs. of original latex, were at follows:—

TABLE XV

Total serum solids <sup>2</sup>	.	.	.	.	.	.	2.91
Ash	.	.	.	.	.	.	0.53
Protein	.	.	.	.	.	.	0.34
Quebrachitol	.	.	.	.	.	.	1.45
Sugar	.	.	.	.	.	.	0.25
Unaccounted for	.	.	.	.	.	.	0.34

A small quantity of a crystalline acid could be extracted from the serum by shaking with ether, but was not examined further. By evaporating the serum, treating it with magnesium oxide, and drawing air through it, ammonia was isolated, and was identified by the preparation of the double platonic chloride.<sup>3</sup>

Dekker<sup>4</sup> records the results of an examination of ammonia-preserved latex from 18-year-old trees. The total solids were 32.4, and the dry rubber obtained by coagulation 29.0 per cent. Hence, the serum solids amounted to 3.4 per cent. of the latex.

<sup>1</sup> *Archief*, 1917, I, 375.

<sup>2</sup> The acetic acid used for coagulation has been deducted.

<sup>3</sup> Gorter states that the latex used was "fresh." It would have been interesting to have known exactly how long had elapsed from its issue from the tree before it was tested for ammonia.

<sup>4</sup> *Meded. Delft*, 1916, p. 529; *Delft Communics.*, pp. 25, 66.

In fourteen days' dialysis 3.2 per cent. could be removed from the latex. The diffusible "nitrogen calculated as protein" was 0.45 per cent. Of this quantity 0.06 was present as ammoniacal nitrogen. The following shows the results of analyses of (a) the total solids from the original latex, and (b) of the air-dried crêpe prepared from the latex by the addition of acetic acid followed by gentle heating.

TABLE XVI

(Percentages)

	Moisture	Ash.	Protein.	Resin
(a) . . . .	2.35	1.60	4.20 <sup>1</sup>	3.20
(b) . . . .	0.50	0.35	3.32	2.40

Two commercial samples of rubber prepared by evaporation of latex, and thus representing the total solids of the latex, were found by Dekker to give the following percentage results:—

TABLE XVII

	Moisture.	Ash.	Protein.	Resin.	Water extract.	Ash after extraction with water.	Protein after extraction with water.
Sample 1 .	2.40	1.43	4.76	—	5.85	0.50	3.54
Sample 2 .	3.61	1.83	4.72	3.62	5.58	0.85	3.32

It will be observed that the greater part of the inorganic constituents and some of the nitrogen in these samples is extractable by water. As regards the composition of the water extract: in two cases the extract contained 38 and 43 per cent. respectively of (ash + protein), the balance presumably consisting largely of quebrachitol.

In the course of an examination of the latex obtained (on—in the case of different groups—from four to nineteen occasions) from eight different groups of trees under different tapping conditions, de Vries<sup>2</sup> found that, despite very marked variation in the rubber-content, and, correspondingly, in the specific gravity of the latex, the specific gravity of the serum remained

<sup>1</sup> Of this amount 0.52 was present as ammoniacal nitrogen.

<sup>2</sup> *Archief*, 1919, 3, 183.

almost constant. While the rubber-content of latex ranged from 18.6 to 44.6 g. per 100 c.cs., and the specific gravity from 0.9983 to 0.9674, the specific gravity of the serum ranged only from 1.0166 to 1.0226. It was found, in general, that when, as under heavier tapping, the percentage of rubber in the latex fell, the total solid matter in the serum also fell (although, proportionately, to a smaller extent), but the inorganic components of the serum rose from a quantity represented by a figure for ash constituting less than one-seventh to a quantity constituting more than one-fifth of the serum solids, with the result that the specific gravity of the serum remained almost constant. The extreme figures (expressed in grams per 100 c.cs. of original latex) for the total-solid-content of the serum were 4.89 and 3.5, and for the ash of the serum 0.585 and 0.87.

#### THE WATER-SOLUBLE CONSTITUENTS OF LATEX

The following additional remarks concerning the character and amount of the water-soluble portion of the latex solids are added. In all probability, of the water-soluble constituents of the latex of *Hevea brasiliensis*, the one present in largest amount is a hydroxy derivative of hexamethylene, known as quebrachitol, and often loosely referred to as a carbohydrate. The presence of polyhydric derivatives of cyclo-hexane in rubber latices was first recognized many years ago. From the liquid enclosed in Gabon (vine) rubber, Girard,<sup>1</sup> by evaporating the liquid and taking the residue up with alcohol, isolated a white, sweet-tasting, crystalline product, which he called dambonitol (dambonite). It was very soluble in water, easily soluble in ordinary alcohol, and slightly soluble in absolute alcohol; it melted at 190°, and, with care, could be volatilized without decomposition. Analysis of the product obtained from alcohol corresponded to the formula  $C_8H_{16}O_6$ , and of the product obtained from water to  $C_8H_{16}O_6, 3H_2O$ . The latter product lost its water at 100°. It would not reduce Barreswil's (Fehling's) solution or undergo alcoholic fermentation. It combined with potassium iodide, when the alcoholic solutions were mixed, beautiful crystals of  $KI \cdot 2C_8H_{16}O_6$  being deposited on cooling. When treated with fuming hydriodic acid, it gave methyl iodide and a product called by Girard dambose, which was somewhat less soluble than dambonitol and crystallized from water without any water of crystallization. Dambrose had a sweet taste and showed the same percentage

<sup>1</sup> C.R., 1868, 67, 820.

composition as glucose. Later, Girard<sup>1</sup> obtained from a sample of Borneo rubber (derived from vines of the genus *Urceola*) a similar, but not identical compound, which he called bornesitol (bornesite). Its melting-point was 175°, and, unlike dambonitol, it was optically active,  $[\alpha]_D$  being +32°. Like dambonitol, it gave methyl iodide and (optically active) dambose on treatment with fuming hydriodic acid.

Girard recognized that dambonitol and bornesitol were methyl derivatives of dambose, but did not further elucidate their constitution. The constitution of dambonitol was established later by Maquenne<sup>2</sup> as dimethyl-*i*-inositol. By the preparation of a tetra-acetyl and of a tetra-benzoyl derivative, Maquenne showed dambonitol to contain, in addition to two methoxy groups, four hydroxy groups. By heating it at 120° with hydriodic acid in a flask attached to a reflux condenser, he obtained from it methyl iodide and dambose; and then, by determining its solubility (a saturated solution at 23.6° contained 12.3 per cent.), the angles of its crystals, and its melting-point (217–218°, uncor.), and by preparing its hexa-acetyl derivative, he established the identity of dambose with *i*(meso)-inositol, the constitution of a sample of which, derived from walnut leaves, he had previously<sup>3</sup> established as *i*-hexahydroxy-hexahydrobenzene. Flint and Tollens<sup>4</sup> examined a sample of bornesitol obtained from the wash-water of a rubber factory. They found its properties to agree with those described by Girard. They definitely established the fact that it contained one methoxy group; thus confirming the presumption that it was monomethyl-*i*-inositol. Later, Weber<sup>5</sup> obtained dambonitol from the latex of *Castilloa elastica*. Weber concluded that the latex probably contained a glucoside,<sup>6</sup> which, however, he was not able to isolate. He obtained a bright yellow, brittle, amorphous mass, which, on treatment with acid, gave dambonitol and a substance, insoluble in water, and crystallizing in fine needles, which he thought was highly probably a coumarin derivative closely related to aesculetin.<sup>7</sup>

A dimethyl-*i*-inositol was isolated by de Jong<sup>8</sup> from the latex

<sup>1</sup> *C.R.*, 1871, **73**, 426.

<sup>2</sup> *Ann. chim. phys.*, 1887, **12** (6), 566.

<sup>3</sup> *C.R.*, **104**, 225, 297.

<sup>4</sup> *Annalen*, 1893, **272**, 288.

<sup>5</sup> *Ber.*, 1903, **36**, 3108.

<sup>6</sup> Spence (*J. Inst. Comml. Res. in Tropics*, Liverpool, 1908, No. 19, 64–75) states that in the latex of *Ficus vogelii* (yielding a low-grade African rubber) there is probably a substance of glucosidal nature, giving on hydrolysis a sugar-like product related to inositol.

<sup>7</sup> A dihydroxy coumarin, derived from the glucoside aesculin occurring in the horse-chestnut.

<sup>8</sup> *Rec. trav. chim.*, 1906, **25**, 48.

of Melaboeai in Sumatra. From the serum of this latex he obtained by evaporation a compound, which, after recrystallization, melted at  $206^{\circ}$ . The compound had the empirical formula  $C_8H_{16}O_6$ , was optically inactive in aqueous solution, and on treatment with hydriodic acid split off two methyl groups and gave inositol. The compound showed great similarity to Girard's dambonitol, but was free from water of crystallization. Also, the tetra-acetyl derivative showed similarity to the tetra-acetyl derivative of Girard's dambonitol.

The latex of *Hevea brasiliensis* contains a monomethyl-inositol which, however, differs from bornesitol in being derived from optically active (*l*-) inositol. The presence of methyl-*l*-inositol,  $C_6H_6(OH)_5(OCH_3)$ , in the latex of *Hevea brasiliensis* was first recognized by de Jong.<sup>1</sup> When the latex was coagulated by means of alcohol, and the alcoholic solution was evaporated, crystals of this body were deposited. Its occurrence was confirmed by Pickles and Whitfield.<sup>2</sup> The latter authors showed the presence of this substance not only in the latex but also in the rubber of *Hevea brasiliensis*—both plantation (smoked sheet) and wild (Fine Hard Para). They found its amount in some samples of smoked sheet to be as high as 2.5 per cent. Methyl-*l*-inositol was first obtained, by Tanret,<sup>3</sup> from quebracho bark,<sup>4</sup> and was called quebrachitol (quebrachite). Quebrachitol melts at  $190-191^{\circ}$  and *in vacuo* boils towards  $210^{\circ}$ , subliming in beautiful needles. It has  $[\alpha]_D - 80.2^{\circ}$ ; requires at  $10^{\circ}$  only 1.7 parts of water for its solution; is somewhat soluble in boiling alcohol, even absolute; is insoluble in ether; has a density at  $0^{\circ}$  of 1.54.<sup>5</sup> The *l*-inositol obtained from it is decidedly more

<sup>1</sup> *Rec. trav. chim.*, 1906, **25**, 48.

<sup>2</sup> *Proc. Chem. Soc.*, 1911, **27**, 54.

<sup>3</sup> *C.R.*, 1889, **109**, 908.

<sup>4</sup> Quebrachitol has more recently been isolated from the leaves of *Grevillea robusta*, A. Cunn. (Bouquetot and Fichtenholz, *J. pharm. chim.*, 1913, **6**, 346; *C.R.*, **155**, 615.)

<sup>5</sup> The chemical behaviour of quebrachitol is given by Tanret as follows: It ferments only under the influence of beer yeast; it has no action on Fehling's solution; it reduces hot ammoniacal silver nitrate; boiling dilute acid or alkali solution do not appear to attack it; it is not precipitated by basic lead acetate; it is precipitated by the ammoniacal acetate if the solution is not too dilute; monohydrated sulphuric acid dissolves it easily when warm, the solution being coloured and quebrachisulphuric acid being formed. The calcium and barium salts of this acid are soluble and non-crystallizable. By adding basic lead acetate, an insoluble salt is obtained, which, when decomposed by sulphuric acid, gives free quebrachisulphuric acid. The acid is *laevo*-rotatory. When heated with acetic anhydride and a fragment of zinc chloride, it gives a crystalline derivative, melting at  $89^{\circ}$ .

Regarding the isolation of inositol from quebrachitol following treatment with hydriodic acid: distil off the methyl iodide and the greater part of the hydriodic acid; pour on to the residue a mixture of alcohol



soluble in water than the common, inactive inositol, being dissolved by 2.3 parts of water at 12°. *l*-inositol melts at 238° (ordinary inositol, 218°) and has  $[\alpha]_D - 55^\circ$ .<sup>1</sup>

*Physiological significance of inositol and its derivatives.*—A few remarks may be added here as to the possible mode of occurrence of inositol derivatives and on the general question of their possible physiological function. Ordinary (*i*; meso) inositol has a very wide distribution in nature, being found in a large number of animal tissues (conspicuously in cardiac muscle and brain) and in a very large number of plants. Although not a carbohydrate, it is not without some relationship to the carbohydrates.<sup>2</sup> Its physiological significance is by no means understood; but the available evidence suggests that inositol is a plastic substance.<sup>3</sup> Maquenne found it to disappear in the young fruits of *Phaseolus* as ripening proceeded. According to Starkenstein<sup>4</sup> it occurs to a greater extent in the organs of young animals than in those of older animals. Feeding experiments<sup>5</sup> have shown that generally only a small proportion of the inositol that may be administered to man

and ether; this precipitates the inositol. Using 5 g. of quebrachitol and 30 g. hydriodic acid (*i. e.* a great excess of the latter), the distilled acid showed noticeably the odour of benzene; that is, the hydriodic acid, as Maquenne had shown, commences to act on the inositol.

<sup>1</sup> De Jong gives  $[\alpha]_D$  as  $-65^\circ$ .

<sup>2</sup> This may be gathered from the following facts: (a) Neuberg ("Beziehung des cyclischen Inosits zu den aliphatischen Zuckern," *Biochem. Zeit.*, 1908, **9**, 551-6) found that, when mixed with phosphoric or boric anhydride, it gave on distillation furfural: a body which hitherto had been known as a derivative of the true carbohydrates. (b) P. Meyer ("Über das physiologische Verhalten von Inosit," *Biochem. Zeit.*, 1907, **2**, 392; 1908, **9**, 45) found ordinary lactic acid in the urine of rabbits fed with inositol. (c) Under the influence of bacteria inositol may be converted into lactic, propionic and butyric acids. This was recognized by the discovery of inositol (Scherer, 1850). The change may be brought about by the agency of putrid cheese or meat. It has been studied by Hilger (*Annalen*, 1871, **160**, 333) and by Vohl (*Ber.*, **9**, 984). Weiss and Rice (*J. Med. Res.*, 1917, **35**, 403; *Chem. Abstr.*, 1917, 1445) found that inositol is fermentable, with gas formation, by *B. lactis aerogens*; although not by *B. acidilactici*. (d) It is proposed to attempt the synthesis of inositol from tetra-acetyl-mucyl chloride (Diel and Löfund, *Ber.*, 1914, **47**, 2351, 2826; J. Müller, *ibid.*, 2654).

<sup>3</sup> Cf., e.g. Mathews (*Physiological Chemistry*, p. 610): "The wide occurrence of inositol in all forms of living cells indicates its connection with some fundamental process in the living protoplasm."

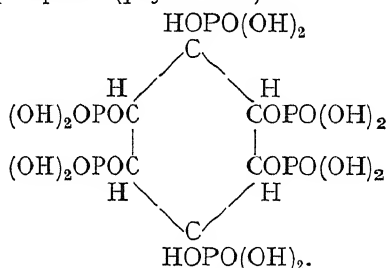
Mellièr ("L'inosite dans le règne organique et en particulier dans les drogues simples et composées. Rôle biochimique de l'inosite," *J. de pharm. et de chim.*, 1908, **28**, 289), from a review of the subject, concludes that inositol (a) is a plastic material, (b) is not a decomposition product, but is to be regarded as a reserve food, (c) bears a close physiological relation to the sugars.

<sup>4</sup> *Zeit. f. Exp. Path. u. Therap.*, **5**.

P. Meyer, *loc. cit.*; Anderson, *J. Biol. Chem.*, 1916, **25**, 391; Anderson and Bosworth, *ibid.*, 399; also Kulz.

or to animals is recovered in the urine. The greater part disappears: whether it is oxidized in the body, or whether it is destroyed by bacteria in the intestines, cannot be said.

In the vegetable kingdom inositol is frequently found in association with phosphoric acid. Winterstein<sup>1</sup> remarked the occurrence in the vegetable kingdom of a phosphorized body which gave inositol as a cleavage product and occurred as a calcium and magnesium salt. This body is known as phytin, and is generally regarded<sup>2</sup> as a calcium and magnesium salt of inosityl-hexaphosphate (phytic acid):—



Accompanying phytin, and capable of effecting its hydrolysis to inositol and phosphoric acid, has sometimes been recognized an enzyme, phytase.<sup>3</sup> Other inositol phosphoric acids have been isolated more recently from vegetable sources.<sup>4</sup> Inosityl-phosphates have also been prepared artificially.<sup>5</sup>

No investigations with reference to methyl inositols, such as those just indicated with reference to inositol itself, have been made. But the investigations on inositol make it at least presumptive that methyl inositols, such as occur in rubber latices, are of metabolic significance, and, in view of the character of the inorganic constituents of latex, may possibly occur to some extent in combination with phosphoric acid, calcium and magnesium. The methylation of inositol was accomplished by Griffin and Nelson<sup>6</sup> by treatment for twenty-four hours with

<sup>1</sup> *Ber.*, 1897, **30**, 2299.

<sup>2</sup> Nueberg, *Biochem. Zeit.*, 1908, **9**, 557; Winterstein, *Zeit. physiol. chem.*, 1908, **50**, 118; Anderson, *J. Biol. Chem.* (various papers). Cf. also Posternack, *C. R.*, 1903, **137**, 202, 337, 439; Plimmer, *Biochem. Jour.*, 1913, **7**, 43.

<sup>3</sup> Suzuki, Yoshimura and Takaishi, *Bull. Agric. Coll.*, Tokyo, 1907, **7**, 503; Anderson, *J. Biol. Chem.*, 1915, **20**, 383, 475.

<sup>4</sup> Inositol mono- and tri-phosphates (Anderson, *J. Biol. Chem.*, 1914, **18**, 425, 441; 1915, **20**, 463, 494). Mostly tri- and penta-phosphates (Rather, *J. Amer. Chem. Soc.*, 1917, **39**, 777). A crystalline salt (with strychnine) of an inosityl-phosphate was first prepared by Clarke (*Trans. Chem. Soc.*, 1914, **105**, 535).

<sup>5</sup> Anderson, *J. Biol. Chem.*, 1913, **12**, 97; etc.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1915, **37**, 1552.

methyl sulphate, followed by acetylation of the product. The methyl inositol obtained, when crystallized from alcohol, had the melting-point  $204^{\circ}$ . This represents the first synthetical preparation of a methyl inositol.

*Other water-soluble constituents of latex.*—Kerbosch<sup>1</sup> found in fresh latex of *Hevea brasiliensis* small but distinct quantities of acetaldehyde and hydrocyanic acid. Quantities, three litres in amount, of fresh latex from 25-year-old trees were steam-distilled, 300 c.cs. of distillate being collected. The distillation was repeated; 30 c.cs. of distillate being collected on the second occasion. In general the latex was originally acid, but when it was not so tartaric acid was added prior to distillation. The distillate gave all the characteristic aldehyde reactions. Acetaldehyde was definitely recognized in the distillate by the preparation from it of the *p*-nitrophenylhydrazone (m.p.,  $128^{\circ}$ ). Three litres of latex gave 70 mg. of the hydrazone, corresponding to about 6 mg. of acetaldehyde per litre. By treating 20 litres of serum, derived from the coagulation, on the same day as that on which the distillation was performed, of fresh latex (from 5 to 6-year-old trees) by means of acetic acid, 1.1 gram of the hydrazone was obtained. In the more concentrated second distillate obtained as above, Kerbosch also recognized clearly the presence of hydrocyanic acid by means of the Prussian Blue reaction. By twice distilling ten litres of fresh serum (from latex coagulated by acetic acid the same day), he obtained a liquid which gave a voluminous precipitate of Prussian Blue. He did not recognize the presence of acetone, and concluded that it did not occur in the fresh latex; although Gorter's demonstration (cf. p. 4) of the presence of phascolunatine in *Hevea* seeds suggested that acetone might accompany hydrocyanic acid in the latex.

Acetaldehyde is a product which has been encountered in nature only rarely. In the case of *Hevea* latex it is not, Kerbosch believes, a product of anaerobic respiration, as in another case had been suggested.<sup>2</sup> Kerbosch also believes that acetaldehyde here is not formed by oxidation (as was suggested in another case of its occurrence<sup>3</sup>), "because of the difficulty or impossibility of explaining why, if such were the case, the caoutchouc hydrocarbon, so easily oxidizable and present in such large quantity, would not also be entirely oxidized." Kerbosch

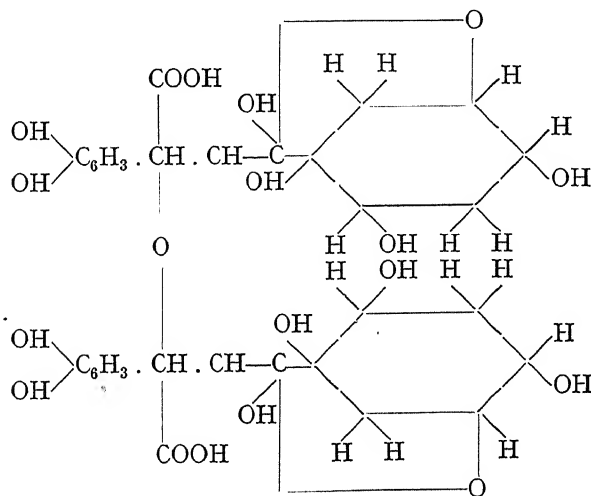
<sup>1</sup> *Meded. over Rubber*, No. iii, 1914, pp. 12-15; *Rubber Recueil*, 1914, p. 361.

<sup>2</sup> Blanksma, *Pharm. Weekblad*, 1913, 46, 1295.

<sup>3</sup> Rosenthaler, *Arch. d. Pharm.*, 1913, 251, 587.

observed that during the period of leaf-fall (tapping being continued) the quantity of acetaldehyde in the latex fell greatly: the distillate no longer gave a precipitate with *p*-nitrophenylhydrazone. The delicate test of Lewins<sup>1</sup> for aldehydes (a blue coloration with a mixture of sodium nitroprusside and piperidine) was still positive but feeble.

Mention may be made here of one or two substances which have been observed in the latex of other rubber trees but not hitherto in that of *Hevea brasiliensis*. Of particular interest is the recognition by Gorter<sup>2</sup> of the presence of chlorogenic acid in the latex of *Castilloa elastica* and in the latex of *Ficus elastica*. A specimen of the acid was isolated from *Castilloa* latex<sup>3</sup> by treating with alcohol, evaporating the filtrate to dryness, extracting with water, and, finally, decomposing the lead salt with hydrogen sulphide. The acid could be detected without isolating it by boiling the latex for one hour with dilute hydrochloric acid, extracting with ether, washing with dilute sodium bicarbonate solution, and treating with ferric chloride solution. A fine violet colour appeared in the aqueous layer on shaking. Chlorogenic acid occurs in coffee, and, as derived from that source, had earlier been investigated by Gorter,<sup>4</sup> who had assigned to it the following constitutional formula:—



<sup>1</sup> Ber., 1899, **32**, 3388.

<sup>2</sup> Rec. trav. chim., 1912, **31**, 281.

<sup>3</sup> 300 g. of latex gave 0.3 g. of chlorogenic acid; m.p. 208°;  $[\alpha]_D^{25}$  — 35.2.

<sup>4</sup> Annalen, 1908, **358**, 327; **359**, 217.

It will be observed that the constituent parts, as it were, of the molecule are 3:4-hydroxycinnamic acid and a tetrahydroxyhexahydrobenzoic acid. The latter bears a relationship to inositol (hexahydroxyhexahydrobenzene). It is not without interest to recall (p. 66) that Weber had recognized in *Castilloa* latex a compound, which he termed a glucoside, yielding a body probably closely related to aesculetin (the lactone of a trihydroxycinnamic acid) and dambonitol (demethyltetrahydroxyhexahydrobenzene).

In the latex of *Ficus elastica* Gorter also recognized the presence of the magnesium salt of a tetrahydroxy-adipic acid. It was identified by distilling the salt in a mixture with ammonium chloride. Pyrrole was evolved. The salt had the formula  $C_6H_8O_8Mg, 3H_2O$ . The free acid derived from it had  $[\alpha]_D^{62} + 36.5^\circ$ . It gave a sparingly-soluble potassium salt, closely resembling potassium disaccharate. It gave a diphenyl-hydrazone (m.p.  $210^\circ$ ) identical with the corresponding compound from *d*-saccharic acid. It was concluded that the acid was identical with *d*-saccharic acid. This acid had not previously been recognized as occurring in nature.

In the latex of twenty-one species of *Euphorbia* examined by Henke,<sup>1</sup> calcium malate was present. The frequent presence of calcium malate in the latex of *Euphorbia* was remarked by Bary.<sup>2</sup> In the latex of *Ficus vogelii* Spence<sup>3</sup> found a noticeably high proportion of magnesium, and obtained a crystalline deposit from the serum which he thought was probably magnesium malate.

*Relation of quebrachitol to vulcanization.*—According to a test made by Stevens,<sup>4</sup> quebrachitol has a retarding effect upon the vulcanization of caoutchouc. One hundred parts of an exceptionally slow curing sample of rubber<sup>5</sup> were mixed with ten parts of sulphur and then vulcanized at  $135^\circ$  for three hours. Another portion of the same sample was treated in the same way except that 3 per cent. of quebrachitol, extracted from latex serum, was added to the mix. The vulcanized products showed the following results:—

<sup>1</sup> *Arch. d. Pharm.*, **24**, 229.

<sup>2</sup> *Vergleichende Anatomie der Vegetations-organe*, Leipzig, 1877.

<sup>3</sup> *J. Inst. Comm. Res. in Tropics*, Liverpool, 1907, p. 64.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1917, **36**, 365.

<sup>5</sup> This sample was prepared by allowing plantation sheet to dissolve in cold benzene over a period of one to two years, and recovering the rubber in an almost nitrogen-free condition (nitrogen-content, 0.05 per cent.) from the solution.

TABLE XVIII

	P <sub>B</sub> .	L <sub>B</sub> .	Coefficient of vulcanization.
Control . . . . .	0.59	1040	1.60
With 3 per cent. quebrachitol . . . . .	0.28	1110	1.32

Both from a consideration of the breaking figures and of the coefficient of vulcanization, the sample containing quebrachitol appears as in a less advanced state of cure than the control sample.

#### VULCANIZATION TESTS

A full discussion of vulcanization testing will be given in Part II of this volume; but with the object of indicating the significance of the terms employed in recording the vulcanization tests quoted in the present Part, it seems desirable to introduce here a few explanatory remarks on the subject of vulcanization tests.

Since rubber is almost invariably employed, not in its raw, but in a vulcanized state, its behaviour on vulcanization, and the properties of the vulcanized product (the vulcanizate), naturally form the main criteria by which the quality of raw rubber is to be judged. Vulcanization is sometimes brought about by treating raw rubber with sulphur chloride ( $S_2Cl_2$ ) dissolved in a suitable solvent; but more generally it is accomplished by mixing the rubber, after rendering it plastic, with sulphur and then heating the mixture (the mix). For technical purposes other materials, in addition to sulphur, are mixed with the rubber prior to vulcanization, but sulphur is the essential vulcanizing agent; and, hence, for the purpose of examining the vulcanizing properties of samples of rubber on a general basis, usually sulphur alone is mixed with the raw rubber. When a mix of rubber and sulphur is vulcanized or "cured," the tensile and other mechanical properties of the product are influenced chiefly by three factors, viz. the percentage of sulphur present, the temperature employed, the time for which the heating is continued. For most testing purposes, it is best to keep the percentage of sulphur and the temperature constant and to make time the variable. As the time of vulcanization (time of "cure") increases, the tensile properties of the product

change progressively, and so does the amount of sulphur entering into "combination" (cf. p. 303) with the caoutchouc.<sup>1</sup> For one particular time of cure, which varies from sample to sample, the tensile properties of the product are at an optimum. And it is found most satisfactory to compare different samples of rubber on the basis of the "optimum cure."

A discussion of the question as to when the tensile properties are in fact to be considered as being at an optimum, and of the procedures by which the optimum cure can be recognized, is given in Part II. In the case of most, but not all, the vulcanization tests quoted in the present Part, the optimum cure was taken as that cure which produced a vulcanizate, which, when stretched in a suitable tensile testing machine, gave a stress-strain (load-elongation) curve which was coincident in position with a standard stress-strain curve adopted as corresponding to optimum tensile properties. The standard curves chosen by different workers all correspond approximately to a maximum in the tensile strength.

The period of vulcanization necessary to give the optimum cure is known as the "time of cure." Speaking broadly, the shorter this period, the better. The stress under which the vulcanizate produced by the optimum time of cure breaks is known as the tensile strength. It is represented here, in kilograms per square mm. of original cross-sectional area of the test piece, by  $P_B$ . The percentage length<sup>2</sup> of the test piece corresponding to  $P_B$  is represented here by  $L_B$ . The product ( $P_B \times L_B$ ) is sometimes called the "tensile product." It represents<sup>3</sup> the actual tensile strength at the moment of rupture. In some cases a further quantity, namely, the "slope" of the stress-strain curve, is given. The characteristic rubber stress-strain curve (Chapter X) is almost straight over its later, "flat" portion. The inclination of this portion of the curve, represented conventionally by the increase in the percentage length between loads of 0.60 and 1.04 kg./mm.<sup>2</sup> divided by 2.5, has been termed the "slope" of

<sup>1</sup> The amount of sulphur in combination with caoutchouc is known, when expressed as a percentage of the rubber, as the "coefficient of vulcanization."

<sup>2</sup> The percentage length represents the actual, total length; the original length being taken as 100. The percentage elongation represents the increase in length; the original length being taken as 100. The terms "length," on the one hand, and the terms "elongation," "stretch" and "extension" on the other hand, are used with considerable looseness in technical literature on rubber; the latter terms not infrequently being used as synonymous with the former term.

<sup>3</sup> On the assumption that Poisson's ratio (cf. Chapter XXI) is 0.5.

the curve. The smaller the inclination (loads being plotted horizontally and elongations vertically), the greater is the resistance which the rubber is offering at the higher loads. Slope bears a relation to sub-permanent set.

The factors kept constant in vulcanizing testing on the lines indicated (*i.e.* percentage of sulphur and temperature) differ somewhat in their magnitude with different workers.<sup>1</sup> In the tests made by Eaton and his co-workers, the percentage of sulphur in the mix is 10 and the temperature of vulcanization is 141°. In the tests made by de Vries and his co-workers, the percentage of sulphur in the mix is 7.5 and the temperature of vulcanization is 148°. The standard optimum curve adopted by de Vries passes through the point: load 1.30 kg./mm.<sup>2</sup>, length 1000 per cent. Tests made by Stevens and by the workers at the Delft Institute, which are quoted in the present Part, were conducted on lines which are different from those indicated above, and the character of which is indicated where the quotations are made.

<sup>1</sup> It may be hoped that in due time steps will be taken (say, by the International Rubber Testing Committee) to bring about at least some measure of agreement as to standard testing mixes. The time appears to be getting ripe for at least some degree of standardization.



## CHAPTER III

### THE RESIN

#### CHEMICAL CHARACTER OF RUBBER RESINS

THAT portion of raw rubber which is soluble in acetone (or alcohol) is commonly denominated "resin." The magnitude of the resin-content varies greatly in the rubber from different botanical sources. It is lowest in rubber from *Hevea brasiliensis*. The amount of resin in dry rubber ranges from such high proportions as 92.8 per cent. in a rubber from a species of *Euphorbia*,<sup>1</sup> about 80 per cent. in samples of Jelutong rubber, and 60 per cent. in some samples of *Castilloa* rubber<sup>2</sup> to less than 3 per cent. in *Hevea* rubber.<sup>3</sup> Owing doubtless to the circumstance that its amount in raw *Hevea* rubber is so small, and that its soft, sticky character places great difficulties in the way of its chemical manipulation, the chemical nature of the "resin" in *Hevea* rubber has never been investigated. The following facts only have been ascertained: (a) It contains oxygen. (b) It is optically inactive. Hinrichsen and Marcusson,<sup>4</sup> who ascertained this fact, found that the resin of *Hevea* rubber was distinguished in this respect from the resin of all other rubber sorts examined. These last in every case showed themselves to be dextro-rotatory. (c) The greater part of the "resin" is saponifiable by alcoholic potassium hydroxide. Hinrichsen and Marcusson found the percentage of matter unsaponified in half-an-hour's treatment with N./2 alcoholic potassium hydroxide to be 15.0 in the case of resin from a sample from wild *Hevea* rubber, and 20.8 in the case of a sample of plantation *Hevea*. All other rubber sorts examined showed a

<sup>1</sup> Vide H. Brown, *Rubber*, London, 1914, p. 51.

<sup>2</sup> *Ibid.*, p. 52.

<sup>3</sup> For considerable data on the resin-content of rubber of different botanical origins, see Terry, *J. Soc. Chem. Ind.*, 1889, 173; 1892, 970; C. O. Weber, *Chem.-Ztg.*, 1894, 1003; Henriques in *Ueber Herkommen und Chemie des Kautschuks*, by Frank and Marckwald, p. 45; Spence, *J. Comm. Res. in Tropics*, Liverpool, 1906, 75; Esch, *Gummiwarenfabrikation*, Dresden, 1906, 21; Hillen, *Arch. d. Pharm.*, 1913, 251, 94; *Bulls. Imp. Inst.*

<sup>4</sup> *Zeit. angew. Chem.*, 1910, 23, 49; 1911, 24, 725; *Mitt. Prüfungsamt*, 1911, 29, 121, 450.

considerably greater unsaponifiable portion. Dekker<sup>1</sup> found similar results. His results are shown in the table below.<sup>2</sup>

TABLE XIX

<i>Hevea</i> rubbers.	Fine Hard Para.	Sheet.	Crêpe.	Oxidized rubber. <sup>3</sup>
Resin-content (per cent.)	3.0	1.8	3.2	60.5
Percentage of resin unsaponifiable . . .	25.4	48.3	22.0	2.4
Other sorts.	Castilloa.	Congo.	Jelutong.	Dyera Crêpe.
Resin-content (per cent.)	18.9	4.4	38.1	7.2
Percentage of resin unsaponifiable . . .	73.7	68.3	83.2	77.8

(d) The iodine number of the resin from a sample of *Hevea*, as determined by Hinrichsen and Marcusson, was 118.0—a figure somewhat higher than that determined for any of the other rubber sorts examined by them. (e) According to C. O. Weber,<sup>4</sup> rubber resin has a marked capacity for combining with sulphur. Henriques<sup>5</sup> did not find that the resin in vulcanized rubber contained sulphur.<sup>6</sup>

Although not in the case of *Hevea*, in that of some other rubbers the chemical character of the resin has been the subject of a certain amount of investigation. The salient points which such investigations have revealed may be mentioned. The most extensively investigated rubber resin is the resin from Jelutong.<sup>7</sup> Alexander<sup>8</sup> obtained from it a body, melting sharply at 161°. Its analysis corresponded to  $C_{25}H_{40}O$ ; and it was considered probable that the body could be written  $(C_{10}H_{16})_5O_2$  and regarded as an

<sup>1</sup> *Meded. Delft*, 1916, p. 527; *Delft Communics.*, p. 49.

<sup>2</sup> The significance of the incomplete saponifiability of rubber resin in relation to the analysis of vulcanized rubber goods is pointed out by the Delft Institute (*Delft Communics.*, p. 49). The unsaponifiable portion will appear as mineral oil.

<sup>3</sup> Cut sheet which had become entirely brittle.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1894, 476.

<sup>5</sup> *Chem.-Ztg.*, 18, 905.

<sup>6</sup> According to L. E. Weber (*I. R. W.*, 1916, 55, 6) a decrease in the resin-content (acetone extract) occurs on vulcanization in the presence of certain inorganic materials, particularly the bases, calcium and magnesium oxides. Dubosc (*Le Caoutchouc*, 1916, 13, 9094) remarks that, in the vulcanization of rubber sorts containing acetates of cholesterol,  $\alpha$ - and  $\beta$ -amyrin and lupcol, metallic oxides would either decompose these substances, freeing sterols and forming metallic acetates, or, more probably, would form acetone-soluble double acetates of cholesterol and the metal. He states that this would explain the increase in acetone extract on vulcanization frequently observed with such rubbers.

<sup>7</sup> Derived from *Dyera* species (mostly *Dyera costulata*). Other designations under which it has been described in the literature are: Djelutong, Pontianak, Dead Borneo, Bresk.

<sup>8</sup> *Gummi-Zig.*, 1904, 18, 867.

oxidation product of caoutchouc hydrocarbon. Hinrichsen and Marcusson,<sup>1</sup> however, found figures for its molecular weight of (in two determinations) 372 and 393. They concluded that it was not an oxidation product of  $C_{10}H_{16}$ , but more probably an alcohol of the cholesterol series. Following Alexander, an investigation of Jelutong resin was made by Sack and Tollens,<sup>2</sup> who obtained from it a body which they regarded as closely related to isocholesterol. Cohen,<sup>3</sup> and subsequently Hillen,<sup>4</sup> have found that Jelutong resin contains large quantities of the acetates of lupeol and of  $\alpha$ - and  $\beta$ -amyrin. Lupeol<sup>5</sup> and the amyrins<sup>6</sup> are among the best-defined resinous substances, and are widely distributed. They are alcoholic in character; and their acetates, benzoates and cinnamates have been prepared. They appear to be sterols or closely related to the sterols. In the Liebermann and in the Hesse-Salkowski cholesterol reactions they give effects very similar to those given by the sterols.<sup>7</sup> Other investigations on Jelutong resin are those of Harries and Paulsen<sup>8</sup> and of Dubosc.<sup>9</sup> In a sample of a *Euphorbia* rubber, containing 92.7 per cent. of resin, Cohen<sup>10</sup> identified  $\beta$ -amyrin acetate and isocholesterol. The latter is contrasted with ordinary cholesterol in being dextro-rotatory. It had previously been isolated by Schulze from wool fat. Hillen found one of the constituents of the resin of Ceara rubber to consist of isocholesterol acetate. It did not give the Liebermann or the Hesse-Salkowski tests. From the resin of Mikindani rubber ("Mozambique Balls") Tschirch and Müller<sup>11</sup> obtained two substances,  $\alpha$ - and  $\beta$ -danielbanes, of the composition respectively  $C_6H_{12}O$  and  $C_{30}H_{48}O$ , which gave colour reactions similar to those given by the sterols.

From a review of what is known concerning the resins of various kinds of rubber and gutta-percha, Hillen<sup>12</sup> concludes that (a) the resins from samples of gutta-percha always contain sterol-like bodies in large quantities, present mostly as esters of

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, **37**, 410.

<sup>3</sup> *Arch. d. Pharm.*, 1907, **245**, 236; *Chem. Zentralbl.*, 1910, I, 1, 651.

<sup>4</sup> *Arch. d. Pharm.*, 1913, **251**, 94.

<sup>5</sup> Likiernik (*Ber.*, 1891, **23**, 3186) and also Sack and Tollens give to lupeol the formula  $C_{30}H_{48}O$ ; Cohen (*Proc. K. Akad. Wetensch.*, Amsterdam, 1906, **9**, 466) gives it the formula  $C_{31}H_{50}O$ , and Jungfleisch and Leroux (*C. R.*, 1907, **144**, 1435)  $C_{30}H_{50}O$ .

<sup>6</sup> See particularly Vesterberg, *Ber.*, 1887, **20**, 1243; 1891, **23**, 3186; also Tschirch, *op. cit.*, pp. 448, 451, 456.

<sup>7</sup> Cf., e.g. Hillen, *loc. cit.*

<sup>8</sup> *Dissert.*, Kiel, 1910.

<sup>9</sup> *Le Caoutchouc*, 1911, **8**, 5574.

<sup>10</sup> *Arch. d. Pharm.*, 1908, **246**, 515, 592.

<sup>11</sup> *Ibid.*, 1905, 141.

<sup>12</sup> "Ueber Kautschuks- und Gutta-percha-Harze," *Dissert.*, Bern, 1913

cinnamic or acetic acid,<sup>1</sup> (b) in an intermediate class, containing such pseudo-rubbers as Jelutong, sterol-like bodies are also for the most part present in large quantities, (c) rubber resins are of a different composition; they are mostly sticky masses; they not improbably consist in large part of oxidation products of the gutta, hardened ethereal oils and resenes; sometimes, however, sterols are present in small quantities. According to Cohen,<sup>2</sup> *Hevea* rubber does not contain lupeol.<sup>3</sup>

According to investigations of Alexander<sup>4</sup> and of Hillen,<sup>5</sup> the resin of Guayule rubber is noticeably different from other rubber resins. It contains no sterol-like bodies. On hydrolysis it gives an acid (m.p. 119°) of the cinnamic series and phenylacetic acid.

*Physiological significance of the rubber resins.*—On the question, so clearly important in regard to the physiology of latex, as to whether the "resin" of *Hevea* latex is in whole or part composed of substances chemically related to the caoutchouc hydrocarbon, little can be said. There has probably always been an inclination to regard the rubber resins as oxidation products of caoutchouc. But, although, as will appear in a later section, caoutchouc is readily oxidizable to acetone-soluble products, it has never been established that the acetone-soluble products naturally present in undeteriorated raw rubber are chemically identical with or similar to such products. The following points may, however, be remarked.

In a number of instances the formula which has been assigned to substances isolated from rubber resins has represented such substances as oxidation products of  $C_{10}H_{16}$ . Spence<sup>6</sup> obtained from the resins of *Ficus vogelii* rubber a substance (m.p. 201–5°), of the formula  $C_{32}H_{52}O_2$ , which, on account of its indifference to chemical reagents, he thought might possibly be represented as  $C_{30}H_{48}(OCH_2)_2$ , *i. e.* as the dimethylether of an oxy-polyterpene related to the class  $(C_{10}H_{16})_n$ , to which caoutchouc belongs.

<sup>1</sup> See, *e. g.* Cohen (*Kon. Akad. van Wetensch.*, Amsterdam, 1906) and van Romburgh (*Ber.*, 1904, **37**, 3440). The former finds  $\beta$ -amyryn acetate in some varieties of gutta-percha. The latter isolated two cinnamic-esters from the resin of a gutta-percha.

<sup>2</sup> *Arch. d. Pharm.*, 1908, **246**, 520.

<sup>3</sup> The author and O. J. Walker have recently isolated from the acetone extract of plantation crêpe small amounts of two well-defined substances. One of these gives the sterol colour reactions. The formula which has been assigned to it is  $(C_{27}H_{46}O_2)_2 \cdot H_2O$ . The other does not give the sterol colour reactions. The formula which has been assigned to it is  $C_{30}H_{50}O_4$ . The two substances are regarded (following Tschirch's nomenclature) as, respectively, a resinol and a resinolic acid.

<sup>4</sup> *Ber.*, 1911, **44**, 2320.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Quart. J. Inst. Comm. Res. in Tropics*, Liverpool, 1907; *Ber.*, 1907, **40**, 999.

Harries<sup>1</sup> obtained from the latex of *Ficus magnolioides* Borci a compound (m.p. 115°),  $(C_{10}H_{16}O)_3$ , and from the latex of *Ficus elastica* a compound (m.p. 195°),  $(C_{10}H_{16}O)_2$ . Spence<sup>2</sup> states that he isolated from the crude resinous extract of a fresh sample of wild *Hevea* rubber a substance identical in all its properties and in its analytical figures with a product obtained by the direct oxidation of a film of *Hevea* caoutchouc exposed to the air for some time, but has not published any experimental results in support of the statement.

Hinrichsen and Marcusson<sup>3</sup> took a sample of *Funtumia* rubber containing 5.22 per cent. of resin showing  $[a]_D + 32.9^\circ$ . They removed the resin completely from the sample; they then allowed the rubber to stand for about a month; and, finally, they extracted the product with acetone and examined the "resin" (in amount 3.1 per cent.) as regards its optical activity. The "resin," which represented an oxidation product of the caoutchouc hydrocarbon, was optically inactive. In view of this result, and of the fact that the resins naturally present in rubber sorts are optically active, Hinrichsen and Marcusson concluded that rubber resins cannot be composed wholly of caoutchouc oxidation products. They suppose rubber resins to consist of two different kinds of constituents, viz. (a) oxidation products of the caoutchouc hydrocarbon, (b) "foreign" substances, without close relation to caoutchouc, such as phytosterol, sugar, etc.

It may be remarked, in connection with Hinrichsen and Marcusson's line of argument, that the resins of *Hevea* form, as has already been stated, an exception to the general rule that rubber resins are optically active. The resin naturally present in *Hevea* rubber resembles caoutchouc oxidation products in being optically inactive. It also, as the observation of Dekker (Table XIX) on a sample of oxidized rubber shows, resembles them in being very largely saponifiable. These considerations are in accord with the view that the resin of *Hevea* rubber is almost entirely composed of caoutchouc oxidation products, although they do not afford any positive evidence in favour of it.

#### MODE OF OCCURRENCE IN THE RUBBER

Discussing the question as to whether the resin of rubber latices forms separate globules in the latex, or whether it is more intimately associated with the caoutchouc, Beadle and Stevens<sup>4</sup> state that, on subjecting samples of *Hevea* latex to microscopic

<sup>1</sup> Ber., 1904, 37, 3842.

<sup>2</sup> Loc. cit.

<sup>3</sup> Loc. cit.

<sup>4</sup> Internat. Cong. Appd. Chem., 1912, 9, 581.

examination, they were not able to detect any differences in the appearance of the globules which could be attributed to differences in composition. They, further, made the following experiment in fractional extraction. Although ether has a coagulating effect on latex, it is possible, "by suitable dilution and adjustment of other details," to extract latex with successive portions of ether in a separating funnel. If resin globules existed separately from caoutchouc globules, it might be expected, in such a series of extractions, that all the resin would be removed in the first extract. They obtained from the latex three successive fractions, representing respectively 11, 11.5 and 6.8 g. of dry solids. On extraction with acetone in a Soxhlet for six hours, the fractions yielded respectively 2.56, 2.44, 2.16 per cent. of resin. So far as this experiment goes, it indicates that separate resin globules do not exist in *Hevea* latex. De Vries finds that if latex is coagulated in two fractions, the first fraction representing not more than 15-25 per cent. of the whole, the acetone extract of the first fraction is about twice as large as that of the second (see Table XXXVIII, p. 133). This observation would appear to indicate a conclusion opposed to that of Beadle and Stevens.

The physical condition of the resin in dry, raw rubber in relation to the caoutchouc has been investigated by Spence and Scott<sup>1</sup> by means of extraction experiments. It has always been recognized that, in order to remove the resin from raw rubber completely, long-continued extraction with successive fresh quantities of acetone (or alcohol) is required. Spence and Scott extracted a sample of rubber repeatedly with a fixed, comparatively-small quantity of acetone, until all the resin was removed. In preliminary extractions, made in order to ascertain the length of time for which it was necessary to allow the boiling acetone to act on the rubber, it was found that, in treating 5 g. of rubber with quantities of 100 c.cs. of acetone, equilibrium was almost reached in half-an-hour. In the actual experiment, which succeeded these preliminary ones, 20 g. of rubber in thin sheets was treated for one hour with successive quantities of 150 c.cs. of acetone. The amounts of resin extracted during each hour are shown in the following table.

TABLE XX

Fraction	1	2	3	4	5	6	7	8	9	10
Per cent. resin extracted	5.34	1.83	0.73	0.36	0.13	0.07	0.061	0.032	0.024	0.017

<sup>1</sup> *Koll. Zeit.*, 1911, 9, 83.

The curve representing these quantities resembles a hyperbola, and is similar to that which Bayliss<sup>1</sup> obtained for the extraction by water of salts (adsorbed) from gelatine. Hatschek<sup>2</sup> remarks that the whole extraction process is an inverted adsorption. From the data of Spence and Scott, Hatschek plots the amount of resin left in the rubber at each point (*i. e.* the concentration of resin in the rubber which is in equilibrium with the concentration of resin in the solvent) against the amount in the solution, and obtains a typical, parabolic adsorption isotherm. Zilchert<sup>3</sup> had previously investigated the extraction with acetone of seventeen rubber sorts, with the object of ascertaining the period of extraction necessary to remove the resin completely in the case of the different sorts. Spence and Scott constructed curves from some of Zilchert's results (including the results for Fine Hard Para). They found all the curves to have the same character as that obtained in their own experiments.

Spence and Scott concluded that at least a part of the rubber resin occurs in the rubber in an adsorbed condition. They refrain from calculating from their results a value for  $\frac{x}{n}$  in the equation  $C = mC^{\frac{x}{n}}$ , because they consider that, in the existing state of knowledge regarding the so-called resinous constituent of rubber, it would be premature to regard the data as doing more than merely establishing the existence of an adsorption between the resinous constituent and the rubber. They observed evidence of the occurrence of selective adsorption of the resinous constituents in the rubber which they examined. (They do not state the sort of rubber examined. Clearly it was not *Hevea*.) The first five fractions contained a gradually diminishing amount of a soft, sticky resin, totally different from the product obtained after the fifth extraction, which was a soft, amorphous, dry material.

#### INFLUENCE OF RESIN ON VULCANIZATION

In Spence's study of the theory of vulcanization there are one or two facts having an incidental bearing on the question as to what influence, if any, resin exerts on vulcanization. These are as follows: The rate of combination of sulphur with pale,

<sup>1</sup> *Biochem. Jour.*, 1906, **1**, 179.

<sup>2</sup> *An Introduction to the Physics and Chemistry of Colloids*, London, 1916, pp. 83, 84.

<sup>3</sup> *Gummi-Zig.*, 1911, **25**, 716.

plantation rubber, which had been extracted for forty hours with hot acetone, and, as a result of the extraction, contained only 0.01 per cent. of resin, was remarkably slow, when vulcanized at 135° in a mix consisting of 90 rubber : 10 sulphur.<sup>1</sup> In the following table are shown the amounts of sulphur which had entered into combination at the end of each hour up to five hours. For comparison there are shown in the same table the corresponding figures for a sample of Fine Hard Para vulcanized under the same conditions.<sup>2</sup> While a strict comparison between the two sets of figures cannot be made, owing to the fact that different samples of rubber were in question, yet, in view of the fact that normal samples of plantation rubber and of Fine Hard Para do not as a rule differ greatly in their rates of vulcanization, the very marked difference in the rate of combination of sulphur shown by the two sets of figures may be taken as indicating that the extraction of resin exercised a retarding influence on the combination of sulphur with caoutchouc.

TABLE XXI

Vulcanization period (hours)	1	2	3	4	5
Combined sulphur (per cent.)					
Resin-free plantation	0.44	0.91	1.40	1.90	2.38
Normal Fine Hard Para	1.14	2.15	2.98	3.75	4.48

It was further observed,<sup>3</sup> in connection with experiments on vulcanization at temperatures below the ordinary vulcanizing temperatures, that practically no combination of sulphur with caoutchouc occurred at the temperatures in question in the case of acetone-extracted rubber, but that the addition of as little as 1 per cent. of the acetone-soluble material led to the combination of sulphur with caoutchouc. Mix *a* consisted of 90 parts of acetone-extracted plantation rubber + 10 parts of pure sulphur. Mix *b* was the same as mix *a* except that it contained 1 per cent. of acetone-soluble constituents. Samples of the two mixes were heated in sealed tubes in glycerol baths at temperatures from 50° to 75° for periods up to 90 days. It was found that even after 90 days' heating at 75° only 0.32 per cent. of sulphur had entered into combination in the case of mix *a*. In the case of mix *b*, quantities (viz. 0.495 and 0.45 per cent. respectively) larger than this had already entered into combination after five days' heating at 75°, or after 80 days' heating

<sup>1</sup> Spence and Young, *Koll. Zeit.*, 1912, 11.

<sup>2</sup> Spence and Ward, *ibid.*, 274.

<sup>3</sup> Spence and Young, *ibid.*, 1913, 13, 265.



at 50°; and the quantity which had entered into combination after 90 days' heating at 75° was 9.36 per cent.

Van Rossem<sup>1</sup> calculated, for a collection of plantation rubber samples, the correlation between the resin-content and the vulcanization coefficient after curing with 7.5 per cent. of sulphur at 147° for 1.5 hours. This statistical treatment of the results obtained on vulcanizing under fixed conditions indicated a low but distinct positive correlation between the resin-content and the rate of combination of sulphur with caoutchouc; the correlation coefficient being, in the case of a group of 214 samples of first latex crêpe,  $+0.270 \pm 0.043$ , and, in the case of a group of (214 first latex crêpes + 101 sheets),  $+0.154 \pm 0.037$ .

Beadle and Stevens<sup>2</sup> made some tests, on samples of *Hevea* and of *Ficus elastica* rubber, in which, in order to avoid the possible effect on the results of the heating involved in the ordinary method of extraction with hot acetone, the removal of resin was accomplished by means of cold acetone. They found that, when vulcanized under the same conditions, the acetone-extracted samples gave, both in the case of *Hevea* and of *Ficus* rubber, much lower figures for the breaking stress than did the untreated samples. Also, the extracted samples deteriorated more rapidly than did the unextracted. The tensile results for the vulcanizates (one week old) obtained from *Hevea* rubber after curing for three hours at 139° and at 135° with 5 per cent. of sulphur are shown below:—

TABLE XXII

	At 139°		At 135°	
	P <sub>B</sub>	L <sub>B</sub>	P <sub>B</sub>	L <sub>B</sub>
Unextracted . . . . .	1.974	1050	0.999	1080
Extracted . . . . .	1.553	850	0.515	710

In a further test cold alcohol was used as the solvent for resin in place of acetone. Over a period of four months 1.94 per cent. of resin, representing about two-thirds of the resin as determined by hot acetone extraction, was removed. The extracted and the unextracted samples were vulcanized in a mix<sup>3</sup> containing

<sup>1</sup> *Bijdrage tot de kennis van het vulcanisatieproces*, Amsterdam, 1916, pp. 124, 129.

<sup>2</sup> *Internat. Cong. Appd. Chem.*, 1912, 25, 581.

<sup>3</sup> The composition of the mix and the conditions of vulcanization are not stated.

some zinc oxide; and when tested after a period of twenty months showed the following results:—

TABLE XXIII

	P <sub>B</sub> .	L <sub>B</sub> .	Percentage elongation at load of 60 g.	Sub-permanent set (per cent.).
Untreated . . .	1.593	630	44.2	3.8
Extracted . . .	0.419	580	76.2	12.6

The authors conclude that extraction of resin, even under the most carefully-regulated conditions, lowers the quality. They add the remark that it cannot be said from the experiments described whether the reduction in quality is due to loss of resin or to some physical effect on the rubber produced by the solvent. As the vulcanization coefficients and the stress-strain curves of the vulcanizates were not determined in this investigation, it is difficult to base on it a definite judgment as to the effect of resin extraction on the rate of cure and on the tensile properties.<sup>1</sup>

Attention may be turned to later results of Stevens and of van Heurn, in the light of which the above results may better be viewed. Stevens<sup>2</sup> obtained, in further experiments on the influence of resin on vulcanization, the results shown in the following table:—

TABLE XXIV

No. of sample.		P <sub>500</sub> .	Sub-permanent set. <sup>3</sup>	Vulcanization coefficients. <sup>4</sup>
1	Untreated rubber . . . .	0.178	25.6	2.86
2	Resin-free rubber . . . .	0.213	18.0	2.71
3	Sp. 2 to which the extracted resin has been returned . . . .	0.184	20.0	3.12
4	Sp. 2+2.5 per cent. Jelutong resin . . . .	0.181	22.0	2.58
5	Sp. 2+2.5 per cent. colophony . . . .	0.156	31.6	2.85
6	Rubber with excess of the insoluble constituent . . . .	0.267	12.4	3.62
7	Sp. 6 acetone-extracted . . . .	0.280	12.8	3.34
8	Protein-free rubber . . . .	0.055	Broke	1.15
9	Sp. 8 acetone-extracted . . . .	0.066	„	1.08

<sup>1</sup> As explained in Part II, breaking figures are an insufficient basis for the comparison of vulcanized rubber samples.

It may be noted, however, that column 3 in Table XXIII indicates that the stress-strain curve of the extracted sample was situated above that of the untreated sample.

<sup>2</sup> *Koll. Zeit.*, 1914, 14, 91.

<sup>3</sup> The percentage elongation remaining immediately after the sample has been stretched five times under a maximum load of 0.2 kg./mm.<sup>2</sup>

<sup>4</sup> Calculated on the resin- and protein-free rubber.

All the samples were derived from the same sheet of unsmoked plantation rubber (sample 1). The resin-content of the original sheet rubber was 2.5 per cent. In the preparation of No. 2, it was reduced by cold acetone extraction to 0.2. Nos. 6 and 8 were prepared, by treatment of the rubber with benzene, so as, respectively, to be rich in, and to be almost free from the vulcanization-accelerating insoluble constituent of rubber (cf. p. 120). All the samples were vulcanized with 7 per cent. of sulphur.<sup>1</sup>

Comparison of No. 2 with No. 1, of No. 7 with No. 6, and of No. 9 with No. 8 shows that the removal of all the resin except 0.2 per cent. had very little influence on the amount of sulphur entering into combination. There is a small reduction in the combined sulphur as a result of the removal of resin; but the reduction is little greater than the experimental error in the sulphur determination. As, however, it appears in all the three pairs of samples just mentioned, it would seem to be connected with the acetone extraction.  $P_{500}$  represents the load necessary to extend the vulcanized sample to a length 500 per cent. of its original length. In view of the fact, which the subsequent work of van Heurn and van Iterson (see p. 90) revealed, that the stress-strain curves for normal and for resin-free samples do not intersect, but are of the same type, the magnitude of  $P_{500}$  may be regarded as indicating approximately the relative position of the stress-strain curves for the different vulcanized samples. Regarding  $P_{500}$  in this manner, it will be seen that, in the case of each of the three pairs of samples mentioned above, the resin-free sample shows a lower stress-strain curve than the normal sample; that is to say, that the effect of resin removal is to produce a state of cure, which, when judged from a tensile point of view, is more advanced than that produced in a comparable normal sample of rubber.

It is of interest to note (sample No. 3) that the restoration of the extracted resin has the effect of bringing the stress-strain curve to the position which it had before their removal (sample No. 1). It is also of interest to observe that foreign resins (samples Nos. 4 and 5) have a similar effect on the tensile properties.

Stevens states that, when kept for several months, rapid deterioration was noticeable in Nos. 2, 4, 5, 7 and 9, the vul-

<sup>1</sup> The temperature and duration of curing are not stated. It is to be presumed that all the samples were cured for the same period of time and at the same temperature.

canizates having become hard and brittle like much over-cured samples; whereas in Nos. 1 and 3 there was no noticeable change. It cannot, however, from this observation alone, be concluded that the removal of the naturally-occurring resin from samples of rubber in itself leads to deterioration of vulcanizates prepared from them.<sup>1</sup>

Further experiments made by Stevens<sup>2</sup> may now be described. In Table XXV are shown the breaking figures and the vulcanization coefficients for two pairs of samples vulcanized with 10 per cent. of sulphur for three hours at 135°. Each pair comprised an unextracted and an extracted sample of the same rubber. The rubber in the case of the first pair was unsmoked sheet, and in the case of the second pair smoked sheet:—

TABLE XXV

	Unsmoked sheet.		Smoked sheet.	
Resin content (per cent.)	Untreated. 1·8	Extracted. Between 0·5 and 0·55	Untreated. 3·9	Extracted. 0·9
Coeff. of vulcn.	3·75	2·86	4·40	3·82
Tested when } P <sub>B</sub> .	1·467	1·020	1·870	1·520
5 days old } L <sub>B</sub> .	1138	1004	1007	983
Tested when } P <sub>B</sub> .	2·060	1·531	2·810	1·470
265 days old } L <sub>B</sub> .	947	836	976	747

Table XXVI shows the results of another similar series of tests, in which three different vulcanization periods were employed:—

<sup>1</sup> The latter of the groups mentioned represents the samples containing the rubber resin. It will be noticed, however, that the former contains, not only the samples freed from rubber resin, but also the samples to which foreign resin has been added. Hence, if the conclusion were drawn that the absence of resin leads to deterioration of vulcanized *Hevea* rubber, and that its presence is favourable to the stability of vulcanized *Hevea* rubber, the proviso would have to be added that this is the case only with the resin occurring naturally in the rubber and does not apply to foreign resin.

In view of the conclusion, stated above, that the resin-free samples were, in regard to their tensile properties, in a more advanced state of cure than the resin-containing samples, it is not unreasonable to suppose that the greater rapidity with which they became brittle is, in part at least, ascribable to their more advanced state of cure (cf. Section on Accelerated Ageing, p. 371).

<sup>2</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 874.

TABLE XXVI

	Untreated rubber.			Extracted rubber.		
Resin-content . . .	1.8			0.7		
Period of vulcn. (hrs.) .	2.5	3	3.5	2.5	3	3.5
Coeff. of vulcn. . .		4.02			3.91	
Tested when $\left. \begin{array}{l} P_B \\ 5 \text{ days old } L_B \end{array} \right\}$ . .	1.130	1.390	1.600	1.000	1.310	1.470
Tested when $\left. \begin{array}{l} P_B \\ 115 \text{ days old } L_B \end{array} \right\}$ . .	1.059	1.008	963	1.021	973	920
	1.340	1.360	1.100	1.060	0.131	0.089
	1046	942	809	890	399	278

Considering the above results firstly, in regard to the effect of removal of resin on the combination of sulphur with caoutchouc, it will be observed that in the case of the last of the three pairs (Table XXVI) the extraction of resin has practically no effect on the vulcanization coefficient, and that in the case of the first two pairs it has the effect of reducing to some extent the amount of sulphur entering into combination. The completeness with which resin was extracted was somewhat different in the different cases, as may be seen from the tables. Considering the results secondly, in regard to the effect of removal of resin on the tensile properties of the vulcanizates, it will be observed that in the case of every cure the resin-extracted sample shows a lower breaking-stress and a smaller length at break than the normal sample. As pointed out in Part II of this volume, it is not possible to form an entirely satisfactory judgment as to tensile properties from a knowledge of the breaking-point alone. The results just noted might signify, not that the stress-strain curve of the resin-extracted sample was lower than that of the corresponding normal sample, but simply that the stress-strain curve of the former broke off earlier, as it were. Consideration of the fact that, as shown by the tensile results made after keeping the samples for some months, the resin-extracted samples move more rapidly than do the normal ones to a condition of brittleness (cf. discussion of Ageing, Part II), together with consideration of other features of the results, make it probable, however, that, in fact, the stress-strain curves of the resin-extracted samples are in all cases lower than the curves of the normal samples; that is to say, that the removal of resin leads to an advance, as regards tensile properties, in the state of cure.<sup>1</sup>

<sup>1</sup> It should be remarked that, in Stevens' own interpretation of his results, the removal of resin is viewed as "not only bringing about gradual

The following experiments on the influence of resin on vulcanization were conducted by van Heurn.<sup>1</sup> Four samples, of 300 g. each, were taken from a specimen of crêpe. The samples were subjected to acetone extraction for four days; the temperature of extraction being 45° during the day-time, and room-temperature during the night. As a result 85 per cent. of the original resin-content of 3.3 per cent. was removed. Mixes as follows were made up of 277.5 g. of rubber: 22.5 g. (*i. e.* 7.5 per cent.) of sulphur.—I. Extracted rubber to which the resin extracted from it had been returned. II. Extracted rubber. III. Extracted rubber to which its own resin together with the resin from the first sample, *i. e.* to which a double quantity of resin had been added. IV. The original, unextracted rubber. After vulcanization at 147° for 1.5 hours, tensile tests were performed. The mean results, obtained from 7–8 Schopper rings, are shown in the following table:—

TABLE XXVII

Sample.	I. (Normal resin-content).	II. (Extracted).	III. (Double resin-content).	IV. (Untreated).
P <sub>B</sub> . .	0.85	0.99	0.775	1.01
L <sub>B</sub> . .	924	881	981	955

A comparison of samples I and IV enables the physical effect of the extraction process, apart from the removal of resins, to be judged. A comparison of samples I, II and III enables the influence of the resin-content of the rubber to be judged. Van

deterioration of what would otherwise have been a correctly-cured sample, but as considerably hastening the deterioration (or perishing) when the specimens had been somewhat over-cured." In the present writer's view it does not necessarily follow from these results that the absence of resin increases the instability of the vulcanizate beyond that which would usually follow the state of cure in question. It is true that the three-hours-cured extracted sample in Table XXVI appears as very unstable—much more unstable than unextracted samples giving similar breaking figures; but the possibility is not excluded that the physical action of the solvent, or more possibly of the heat accompanying its use, may be a factor in the instability. Heat had been used in conducting the extraction of at least part of the extracted samples given in Tables XXV and XXVI.

Stevens compared in the litharge mix, shortly to be mentioned, rubber which had been extracted with cold acetone with rubber which had been extracted with hot acetone, and did not find any appreciable difference in the tensile properties of the two samples when vulcanized. As, however, the samples were very much under-cured, and as the mix was a mineralized one containing litharge, it would not be safe to assume that the cold- and hot-extracted samples would behave identically in the rubber-sulphur mix which is in question in Tables XXV and XXVI.

<sup>1</sup> *Meded. Delft*, 1916, p. 407; *Delft Communics.*, p. 194.

Heurn concluded merely that the presence of resin reduces the breaking load. It will be observed that this conclusion is opposed to Stevens' results, although the results both of Stevens and of van Heurn agree in finding the length at break to be increased by the presence of resin. A further treatment of van Heurn's results by van Iterson<sup>1</sup> illuminates considerably the question of the effect of resin on vulcanization.<sup>2</sup> Van Iterson com-

pared the stress-strain curves for samples I-IV by bringing them together in a single diagram—shown in Fig. 3.

This diagram makes it clear that the effect of the presence of resin is to cause the stress-strain curve to lie higher on the paper than it would do in its absence; that is to say, to lead to a less advanced state of cure in regard to tensile properties. At a given load the elongation is greater in the presence of resin than in its absence, and is greater the larger the amount of resin present. The results of Stevens given in Table XXIV are in entire agreement with this conclusion.

It is interesting to note from a comparison of the curves for samples I and IV, that the restoration to the extracted rubber of the resin which

had been removed from it leads to a stress-strain curve, which is practically coincident in its course with that of the stress-strain curve from the original, untreated rubber, but which breaks off short. The effect of the action of the solvent and of the heat accompanying its use appears to be comparable with the effect of excessive mastication of rubber on the mixing rolls (cf. 292).

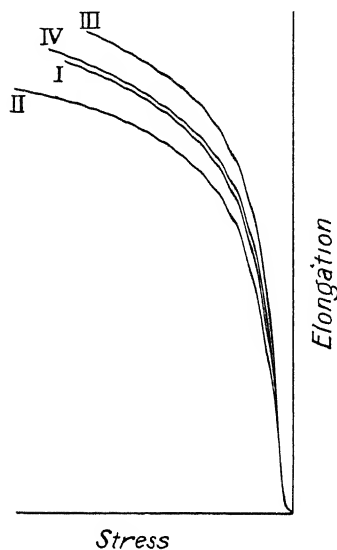


FIG. 3.

- I.—Extracted rubber + resin.
- II.—Extracted rubber.
- III.—Extracted rubber + double the quantity of resin.
- IV.—Original rubber.

<sup>1</sup> *Delft Communics.*, pp. 197-8.

<sup>2</sup> And, incidentally, emphasizes the value, noted in Part II, of considering the stress-strain curves when comparing vulcanizates.

*Conclusions.*—In the light of the foregoing discussion<sup>1</sup> concerning the influence of resin on vulcanization, the following statements, which, although provisional and subject to modification or amplification as a result of future research work, may be made with some degree of confidence:—

(a) The removal of the resin, at least to the extent that the amount left is only 0.2 per cent., has little or no influence on the rate of combination of sulphur with caoutchouc in a mix, consisting of rubber and sulphur only, and cured at the usual vulcanization temperatures.<sup>2</sup> (b) The removal of resin affects the stress-strain relations of the vulcanizates produced, from rubber and sulphur only, under any given curing conditions, in the sense of bringing the stress-strain curve down the paper; that is to say, of reducing the elongation corresponding to any given load.

*Resin and vulcanization in the presence of litharge.*—It appears that the rubber resin bears a much more important relation to the vulcanization of mixes containing litharge than it does to the vulcanization of simple rubber-sulphur mixes. L. E. Weber<sup>3</sup> found that *Hevea* sheet the resin-content of which had, as a result of extraction for fifteen hours with hot acetone, been reduced from 3.6 to 0.3 per cent., "could not be vulcanized" in a mix of the composition: rubber 50, litharge 6.2, sulphur 3.1, whiting 40.7 per cent. When heated for one hour at 140° it showed a tensile strength of less than 20 lb. in.<sup>2</sup>; whereas the unextracted rubber, or rubber to which extra resin had been added, developed its maximum strength at a shorter cure.

Stevens<sup>4</sup> investigated further the relation of resin to vulcanization in this mix. He found that, while it could hardly be said that the resin-free rubber "could not be vulcanized" in this mix, the absence of resin certainly retarded the vulcanization very greatly. The results are shown in the following table. Samples 1, 1a, 2 and 3 form one series, and samples 1', 2' and 3' another. The

<sup>1</sup> It should, perhaps, be remarked that the foregoing discussion has been conducted from the point of view propounded in Part II, which the most recent researches into the principles of vulcanization testing has suggested, and which differs somewhat from the point of view of the authors whose work forms its basis.

<sup>2</sup> It should be noted that the conditions under which the results of Spence and Ward (p. 373), as to the great influence exerted by resin on the combination of sulphur and caoutchouc were obtained, viz. removal of the resin so complete that only 0.01 per cent. remained and vulcanization temperatures much below the usual ones, are not contemplated in the above statement.

<sup>3</sup> *Internat. Cong. Appd. Chem.*, 1912, 9, 95.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1916, 35, 874.



rubber in the former series was unsmoked sheet, and in the latter smoked sheet. The rubber in Nos. 1 and 1' had been extracted with cold acetone; in No. 1a with hot acetone; in Nos. 2 and 2' it had not been treated; Nos. 3 and 3' contained untreated rubber to which additional resin (derived respectively from the extraction of Nos. 1 and 1') had been added. Vulcanization was conducted at 132°. The breaking figures were taken seven days after vulcanization.

TABLE XXVIII

(The figures in brackets represent coefficients of vulcanization)

No.	Resin-content (per cent.).	20 mins. cure $P_B \times L_B$ .	25 mins. cure $P_B \times L_B$ .	30 mins. cure $P_B \times L_B$ .	40 mins. cure $P_B \times L_B$ .
1	0.55	Too weak to test	Too weak to test	$0.276 \times 746$ (0.58)	$0.314 \times 702$
1a	0.50	do.	do.	$0.296 \times 711$ (0.58)	$0.284 \times 667$
2	1.8	$0.726 \times 713$	$0.771 \times 709$ (1.02)	$0.750 \times 707$ (1.14)	$0.802 \times 718$ (1.36)
3	2.3	$0.887 \times 677$	$1.015 \times 688$ (1.36)	$0.857 \times 676$ (1.42)	$0.996 \times 688$
1'	0.9	Too weak to test	Too weak to test	$0.240 \times 665$	$0.274 \times 642$
2'	3.9	$1.252 \times 656$	$1.236 \times 667$	$1.212 \times 660$	$1.227 \times 642$
3'	4.8	$1.385 \times 654$	$1.446 \times 659$	$1.386 \times 550$	$1.322 \times 665$

It is clear that the effect of the presence of resin is to increase the rate of cure in this compound. The vulcanizates from Nos. 3 and 3' are, it may be seen, in a more advanced state of cure than corresponding vulcanizates from Nos. 2 and 2'.

By means of auxiliary experiments, Stevens showed that the special relation of resin to the vulcanization of a mix of the above composition was conditioned by the presence of litharge. The whitening could be omitted without affecting the character of the results. Stevens concluded that the susceptibility of mixes containing litharge to the removal of resin is in accord with the views of Esch and Auerbach<sup>1</sup> as to the mode of action of litharge. In this view the accelerating influence of litharge is due to the oxidation of the oxide and sulphide to the sulphate of lead, by means of oxygen supplied by the resin, having the result of raising the temperature of the mass during vulcanization.

#### NITROGEN-CONTENT OF THE RESIN

An aspect of the acetone extract which has not hitherto been explored, but which is probably of considerable significance in regard to the relation of the acetone extract to vulcanization,

<sup>1</sup> *Gummi-Markt*, 1911, p. 123.

is the inclusion of nitrogenous compounds in the extract. Passing mention is made of this aspect in the course of Spence's vulcanization researches. In a footnote, Spence and Kratz<sup>1</sup> write as follows: "We may here mention a point which other workers have not observed or have not taken into consideration in their investigation of the acetone extract. This is the circumstance that the extract from *Hevea* rubber contains a considerable quantity of nitrogen, which is the cause of certain definite properties of this extract and of the rubber. Whether the nitrogenous constituent of the acetone extract is responsible for properties of the so-called acetone-soluble impurity of *Hevea* rubber, other than those (namely, in the first place, its preservative function against deterioration of the hydrocarbon, and, in the second place, its catalytic function in vulcanization) which for some years we have recognized as its direct effects, can only be decided by further investigation." Spence has not, however, published any data on the nitrogen-content of the acetone extract. The presence of nitrogen in the acetone extract was confirmed by Dekker.<sup>2</sup>

The manner in which Dekker was led to conclude that nitrogen goes into the acetone extract of *Hevea* rubber was by a comparison of the nitrogen-content of samples of rubber before and after extraction. The following shows his results with four samples of *Hevea* rubber. Nos. 1 and 2 are crêpes, No. 3 is sheet, and No. 4 is Fine Hard Para.

TABLE XXIX

No.		1	2	3	4
Nitrogen	Originally	3.80	2.43	3.10	2.10
calculated	After acetone extraction	3.48	2.25	3.01	1.77
as protein	In acetone extract (by diff.)	0.32	0.18	0.09	0.33

In the case of samples of Congo, Manicoba and Castilloa rubber nitrogen was determined directly in the acetone extract.

As will appear later, many nitrogenous substances have a strongly accelerating effect on the vulcanization of rubber. It is of interest to observe that the acetone extract tends to be exceptionally high in raw rubber prepared according to certain methods which result in a rapidly vulcanizing product. Dekker<sup>3</sup> found the acetone extract to be higher in rubber prepared (from preserved latex) by evaporation of the latex than by coagulation

<sup>1</sup> *Koll. Zeit.*, 1914, 14, 268.

<sup>2</sup> *Meded. Delft*, 1916, p. 506; *Delft Communic.*, p. 55.

<sup>3</sup> *Meded. Delft*, 1916, p. 529.

with acetic acid. In one series of samples the acetone extract of a sample prepared by simple evaporation was 3.13 per cent., and of a sample prepared by evaporation, washing and crêping 3.68 per cent., as against 2.00 in a sample coagulated by acetic acid and crêped. In another series the corresponding figures were 3.20 and 3.00 as against 2.40. The acetone extract from the samples prepared by evaporation contained a noticeable proportion of material soluble in water.

In the Ceylon vulcanization tests it was found that rubber which had been allowed to "mature" while wet (cf. Chap. VIII.),<sup>1</sup> and which, when dry, vulcanized, on account of the maturation, exceptionally rapidly, gave high figures for the acetone extract. The following table shows results obtained in four series of experiments. Each figure represents the mean figure for three samples.<sup>2</sup>

TABLE XXX

		Resin (per cent.).	Protein (per cent.).	Time of cure. <sup>3</sup>
SERIES I.				
Normal sheet	. .	2.40	2.36	65 min.
Matured sheet	. .	3.92	1.89	38 "
SERIES II.				
Normal sheet	. .	3.01	2.41	70 "
Matured sheet	. .	3.36	2.16	45 "
SERIES III.				
Normal sheet	. .	2.48	2.12	91 "
Matured sheet	. .	3.23	1.99	50 "
SERIES IV.				
Normal sheet	. .	2.40	2.18	100 "
Matured sheet	. .	2.94	1.98	73 "

It is interesting to observe that the effect of maturation has been to reduce the "protein" and increase the acetone extract. Maturation connotes, substantially, bacterial decomposition of the protein of the coagulum with the formation of simple nitrogenous substances, which are presumably soluble in acetone. Grantham (p. 191) has shown that it usually leads to a reduction of the total nitrogen in the rubber. (Unfortunately it is

<sup>1</sup> Maturation was brought about by rolling the sheet up while wet. (The samples which were subjected to maturation contained creosote, except in series IV, where they contained formaldehyde; the normal sheets did not. It was, however, established (*Dept. Agric. Ceylon, Bull.*, No. 35, 1918, p. 12) that the high acetone extract was not due to the inclusion of creosote in the "resin.")

<sup>2</sup> *Dept. Agric. Ceylon Bull.*, No. 27, 1916, *Bull.*, No. 35, 1918.

<sup>3</sup> At 50 lb. steam pressure, in the mix, 90 rubber, 10 sulphur.

not stated in connection with the experiments to which Table XXX refers whether for the analytical determination of "protein" the original raw rubber or the rubber after acetone extraction was taken.)

Fol,<sup>1</sup> from a study of the relations of resin to the viscosity of rubber in the case of samples of *Castilloa* rubber with resin-contents ranging from 18.9 to 37.0 per cent., concluded that resins have the effect of producing a diminution of viscosity.

#### TACKINESS. OXIDATION

Subjects which may with some degree of appropriateness be discussed at this point, are (a) the oxidation of caoutchouc by air or oxygen to products which resemble the rubber resin, at all events in being soluble in acetone; (b) tackiness. The occurrence of oxidation of caoutchouc and the occurrence of tackiness are often associated. Whether they are causally connected will be the subject of discussion.

*Oxidation products.*—The earliest analysis of a rubber oxidation product was made by Adriani,<sup>2</sup> whose material showed on analysis 11.4 per cent. of oxygen. Spiller<sup>3</sup> extracted, by means of alcohol, from the "perished" rubber of an old piece of rubber-coated fabric, a product giving the analytical figures: carbon 64.00, hydrogen 8.46, oxygen 27.5 per cent. Hofmann<sup>4</sup> had shortly before obtained from a deteriorated sample of gutta-percha an oxygenated product which gave similar analytical figures. He had stated that he was "far from believing that these oxygenated substances are definite [*i. e.* single] chemical compounds," and had refrained from working out an empirical formula on the basis of the analytical figures. Spiller similarly refrains in regard to his oxygenated product. Later, C. O. Weber<sup>5</sup> pointed out that Spiller's figures agree approximately with the formula  $C_{30}H_{48}O_{10}$ , *i. e.*  $[(C_{10}H_{16})_3 + 5O_2]$ . Acetone-soluble products arising from the oxidation of caoutchouc have often been denominated "Spiller's resin." Miller<sup>6</sup> exposed 500 grains of Para rubber in the shape of thin strips to the action of light and air for nine months, and observed that at the end of this period the weight had increased by 2.8 per cent., and that the material yielded 11.81 per cent. of a soft, viscous "resin"

<sup>1</sup> *Internat. Cong. Appd. Chem.*, 1912, **9**, 71; *Meded. Delft*, 1916, p. 321.

<sup>2</sup> *Jahresb. der Chem.*, 1850, 520; 1860, 496.

<sup>3</sup> *J. Chem. Soc.*, 1865, **18**, 44.

<sup>4</sup> *Ibid.*, 1861, **13**, 87.

<sup>5</sup> *J. Soc. Chem. Ind.*, 1900, **19**, 216.

<sup>6</sup> *J. Chem. Soc.*, 1865, **18**, 273.

containing 23.23 per cent. of oxygen. Herbst<sup>1</sup> dissolved 6.004 grams of purified Para rubber in 600 c.cs. of benzene, and passed dried air through the solution while it was maintained at the boiling-point for 140 hours under reflux. The product obtained after removal of the solvent weighed 6.735 g. By extracting with petrol ether, the greater part went into solution. The petrol ether solution gave on evaporation 5.818 g. of a light red-brown syrup, the analysis of which indicated that it had the formula  $C_{10}H_{16}O$ . The part insoluble in petrol ether was later divided by solution in benzene followed by precipitation with petrol ether into two fractions weighing 0.115 and 0.15 g. Both of these fractions gave on analysis figures corresponding to  $C_{10}H_{16}O_3$ .

Peachey<sup>2</sup> studied the absorption of oxygen by thin films of rubber maintained at 85° in an atmosphere of oxygen. In four successive experiments the weight of oxygen absorbed corresponded to 4.12, 4.16, 4.14 and 4.01 atoms per  $C_{10}H_{16}$ -residue. Later, Peachey and Leon<sup>3</sup> recognized that some carbon dioxide was produced in the reaction. On repeating the experiments, it was still found that the number of atoms of oxygen taken up by  $C_{10}H_{16}$  approximated to four (results in four experiments: 4.16, 4.11, 4.27, 3.97); but it was found that approximately one-quarter of an atomic proportion of carbon was oxidized to carbon dioxide per  $C_{10}H_{16}$ .

Under other conditions of oxidation Peachey and Leon obtained other products. The conditions in question were the exposure of 50 g. of extracted rubber continuously for six months in shallow dishes to an atmosphere of oxygen in an oven at 85°; the oxidized material formed on the surface being removed by extraction with alcohol every forty-eight hours. By treatment with a variety of solvents and precipitants, Peachey and Leon separated from the oxidized material four products, of clearly different properties, to which they assigned the formulæ respectively of  $C_{16}H_{26}O_3$ ,  $C_6H_9O_2$ ,  $C_{11}H_{16}O_4$ ,  $C_{11}H_{16}O_4$ . There does not appear to be any proof that these products represent chemical individuals.

On investigating somewhat further certain samples of *Hevea* crêpe, in which a rapid oxidation of caoutchouc was occurring, and concerning which some data have already been published,<sup>4</sup> the present writer found that the increase in weight (represent-

<sup>1</sup> Ber., 1906, 39, 523.

<sup>3</sup> Ibid., 1918, 37, 55.

<sup>2</sup> J. Soc. Chem. Ind., 1912, 31, 1103.

<sup>4</sup> Koll. Zeit., 1913, 12, 197.

ing the oxygen entering into combination <sup>1</sup>) when compared with the increase in the amount of acetone extract indicated that the amount of oxygen entering into combination was two atoms for each  $C_{10}H_{16}$  unit. In an investigation <sup>2</sup> of the oxidation of caoutchouc under the catalytic influence of copper salts, a comparison of the increase in weight at any point with the increase in the acetone extract up to the same point has, also, indicated that two atoms of oxygen combine with each  $C_{10}H_{16}$  unit.

It thus appears that the product or products of oxidation vary considerably in their composition according to the method of oxidation employed. The formulæ of Herbst's two bodies have already been mentioned; Peachey's product corresponds to  $C_{10}H_{16}O_4$ , and the present writer's to  $C_{10}H_{16}O_2$ . It would, however, be hazardous to state that the products in question represent chemical individuals.

*The oxidation of caoutchouc as an autoxidation.*—Wo. Ostwald <sup>3</sup> points out that the curves connecting oxygen absorption with time obtained by Peachey have the S-form characteristic of so-called autocatalytic processes, the most thoroughly investigated example of which is the oxidation of linseed oil. <sup>4</sup> In linseed oil autoxidation the catalyst concerned is a labile inter-product (possibly an organic peroxide) rich in oxygen. Gorter, <sup>5</sup> also, has investigated the absorption of oxygen (from air) by a thin film of rubber. (The rubber employed was a vine-rubber, with a tendency to become tacky.) He found that there was an initial "lag" in the absorption of oxygen. 0.2 g. of rubber was deposited as a film on the inner surface of a 120 c.c.-distilling flask, and was exposed to diffused daylight in the tropics. During the first six days no absorption of oxygen occurred. Absorption then proceeded continuously. Gorter concluded that the process was an autoxidation, and pointed out its analogy to the behaviour of linseed oil as determined by Genthe. Peachey observes that he found an extract of his resinous product to liberate iodine from potassium iodide slowly, but eventually very markedly. Kirchhof <sup>6</sup> has developed the view of the oxidation of caoutchouc as an autoxidation process. In an experiment he exposed resin-free Para rubber for one year to light and air. He then found

<sup>1</sup> The assumption is made that no loss of carbon or hydrogen accompanies the oxidation.

<sup>2</sup> Unpublished. By the author, in conjunction with O. J. Walker.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1913, **33**, 179.

<sup>4</sup> Genthe, *Zeit. angew. Chem.*, 1907.

<sup>5</sup> *Meded. over Rubber*, No. II, 1912; *Rubber Recueil*, 1914, p. 385.

<sup>6</sup> *Koll. Zeit.*, 1913, **13**, 49.

that, on treating 25 c.cs. of a benzene solution containing 1.15 g. of the product with potassium iodide for twelve hours in the dark, with frequent shaking, iodine was liberated to an amount corresponding to 2.3 c.cs. 0.04-N. sodium thiosulphate solution. Also, potassium permanganate was rapidly decolorized by the product. Kirchhof concluded that peroxide-like compounds were present in the product. He suggested that an unstable peroxide,  $C_{10}H_{16}O_2$ , was an intermediary in the oxidation of caoutchouc. He supposed that Herbst's products arose as follows:—

1.  $C_{10}H_{16} + O_2 \rightarrow C_{10}H_{16}O_2$ .
2.  $C_{10}H_{16}O_2 + C_{10}H_{16} \rightarrow 2C_{10}H_{16}O$ .
3. The latter compound is able on account of its unsaturated valencies to attach further molecular oxygen, giving  $C_{10}H_{16}O_3$ .

Kirchhof<sup>1</sup> also investigated the action of 3 per cent. hydrogen peroxide on raw rubber. He found it to produce tackiness on the surface, and recognized the presence of a peroxide in the washed product.

*Oxidizability of caoutchouc.*—It has been noticed by many workers that the caoutchouc of raw *Hevea* rubber which has been deprived of its resin is much more susceptible to oxidation than the caoutchouc of rubber with its normal resin-content. In Peachey's experiments on heating thin films of rubber in oxygen, it was found that, although the presence of resin exerted little influence on the amount of oxygen finally absorbed, it greatly affected the rate at which it was absorbed. With resin-free rubber oxidation started a few hours after heating began; with resin-containing rubber a heating period of ten to twenty times as long was required before appreciable absorption of oxygen began. Kirchhof<sup>2</sup> reported the following results for two samples of plantation rubber, in the form of thin sheets, heated at 100° for eighty hours in a current of dry air.

TABLE XXXI  
(Percentage increase in weight)

	No. 1.	No. 2.
Resin-containing sample . . . .	0.2	0.1
Resin-free sample . . . .	4.0	3.8

The readiness with which samples of rubber, which had been prepared from latex according to different methods, underwent oxidation was investigated by Kerbosch.<sup>3</sup> Each sample was

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Meded. over Rubber*, No. III, 1914.

prepared from 5 c.cs. of latex derived from twenty-five-year-old trees and was dissolved in 100 c.cs. of benzene in a 140 c.cs. distilling flask; the benzene was removed by distillation, so as to leave the rubber deposited as a thin film on the inside of the flask. The rubber was finally dried at 105°; the neck of the flask was drawn out and sealed, and the (lengthened) side-arm was arranged to project downwards into mercury. The progress of oxidation was determined by following the rise of the mercury level as the oxygen of the air was absorbed. The samples were exposed to sunlight for a few days (cf. Gorter, p. 97) and were then left in diffused daylight for more than a month. The experiments made were as follows:—

*Series I.*—Sample *a* coagulated by acetic acid, rolled out as sheet, and dried at 100°; *b* coagulated by acetic acid, dried by smoking for eight hours; *c* coagulated by alcohol, otherwise as *a*; *d* coagulated by means of smoke at 80–90°, following as nearly as possible the Brazilian procedure; *e* the latex simply evaporated at 105° to constant weight; *f* latex dried *in vacuo* over sulphuric acid. *Results.*—The group *a, b, c* was sharply contrasted with the group *d, e, f*. The samples in the latter group underwent practically no oxidation. During thirty-two days' exposure to diffused daylight, the rise in the mercury level was, in the case of all three samples, only about 20 cms.; whereas in the case of the samples in the former group it was as follows: *a* 280, *b* 265, *c* 210 cms. (approximately). At the end of the exposure just mentioned, the slow-oxidizing samples, *d, e, f*, were treated with water at room temperature, in order to remove soluble constituents. As a result of this treatment, further exposure to light caused these samples to absorb oxygen at a rate similar to that at which the samples *a, b, c* had absorbed it. The samples in the above series were all prepared from the same batch of latex.

*Series II and III.*—In each series the samples were prepared from the same lot of latex. The practical absence of oxidation in rubber prepared by the evaporation of latex at 105° was confirmed; and it was found that if rubber so prepared were, previous to exposure, extracted for 3 × 24 hours with water at 25–30° it oxidized as rapidly as did acetic acid-coagulated sheet rubber.

*Series IV.*—It was concluded that quebrachitol had no preventive influence on the absorption of oxygen. Acetic acid-coagulated sheet, which had been soaked for 3 × 24 hours in a



5 per cent. aqueous solution of quebrachitol, was found to absorb oxygen as quickly as the original, unsoaked sheet. The experiment would not, however, appear to give a sufficient proof of the absence of preventive influence on the part of quebrachitol, as it is not likely that any considerable amount of quebrachitol was actually introduced into the rubber by the treatment followed.<sup>1</sup>

*Series V.*—It was found that egg-white prevented oxidation. A sample of acetic acid-coagulated sheet to which, while it was in solution in benzene, ten drops of fresh egg-white was added, absorbed oxygen only at the same (slow) rate as a sample of rubber prepared from the same latex by evaporation at 105°; whereas acetic acid-coagulated sheet to which no egg-white had been added oxidized rapidly as in previous experiments.

#### TACKINESS. DISAGGREGATION

The subject of "tackiness" in raw rubber is a subject the discussion of which has been closely associated with the discussion of the oxidation of caoutchouc. "Tacky" <sup>2</sup> rubber exhibits a condition of stickiness, and in severe cases may be semi-fluid. Low-grade African rubbers, which, prior to the advent of plantation rubber, formed an important proportion of the raw rubber on the market, frequently exhibited this objectionable condition; and, in its early days, the plantation product also showed a noticeable proportion of samples which were tacky. Now, however, cases of tackiness in plantation rubber (except in the lowest grades <sup>3</sup>) are extremely rare. Hence a discussion of the causes of tackiness has not now the degree of practical importance which it would have possessed some years ago. On account, however, of its association with the discussion of oxidation in rubber, the question of tackiness is not without interest.

Two main views concerning the causes of tackiness in rubber have been expressed. One of these regards tackiness as dependent on oxidation. The other regards it as primarily due to a reduction in the state of aggregation of the caoutchouc; and considers any oxidation which may accompany tackiness as a secondary phenomenon arising from the circumstance that the

<sup>1</sup> The rubber was dried before being soaked.

<sup>2</sup> German, *leimig*; French, *poisseu*; Dutch, *pekkig*.

<sup>3</sup> Bark shavings and earth rubber. These grades form only a small proportion of the crop; and tackiness is quite rare in bark shavings and not frequent in earth rubber.

precedent reduction in the state of aggregation is favourable to the occurrence of oxidation. Protagonists of the former view have been Fickendey,<sup>1</sup> Gorter<sup>2</sup> and others, and of the latter view Spence,<sup>3</sup> Whitby<sup>4</sup> and others. The most recent investigations on the question—the investigations of van Rossem,<sup>5</sup> while supporting the view that disaggregation is the primary cause of tackiness, nevertheless, by showing that the disaggregation is strongly catalyzed by the presence of oxygen, indicates the ground upon which a reconciliation of the two views is to be achieved. Kirchhof appears at first<sup>6</sup> as a supporter of the oxidation view, but later<sup>7</sup> adopts the disaggregation view.

Spence concluded from experiments on samples of *Funtumia* rubber, which were tacky owing to the use of sulphuric acid in coagulation, that the resin-content, the oxygen-content, and the capacity for adding on bromine were not noticeably different in tacky and in sound samples, and that tackiness was a physical phenomenon dependent upon a reduction in the state of aggregation of the caoutchouc.

Fickendey concluded that oxygen was essential to the occurrence of tackiness. He urged that the fact that tackiness always starts at the surface of the rubber and never in the centre of it favoured the view that it was due to oxidation. He found that when rubber was sealed in tubes containing hydrogen, nitrogen, or carbon dioxide and exposed for several weeks, it did not develop tackiness; but that, if sealed in tubes containing air or oxygen, it became tacky, and that, on opening, under water, tubes in which rubber had been sealed up in air or oxygen, the water rose in the tubes. When oxygen was used, the residual gas was pure oxygen: it did not contain carbon dioxide. Fickendey observed that raw rubber became tacky when immersed in hydrogen peroxide and exposed to sunlight, but did not do so if kept in hydrogen peroxide in the dark for some weeks. He stated, further, that the advance of tackiness in already-tacky samples came to a standstill even in sunlight if oxygen were excluded.

<sup>1</sup> *Koll. Zeit.*, 1911, **11**, 81.

<sup>2</sup> *Meded. over Rubber*, No. II, 1912, p. 54; *Rubber Recueil*, 1914, p. 385.

<sup>3</sup> *Koll. Zeit.*, 1909, **4**, 70.

<sup>4</sup> *Ibid.*, 1913, **12**, 190.

<sup>5</sup> *Rubber Industry*, 1914, p. 149; *Meded. Delft*, 1916, p. 465.

<sup>6</sup> *Koll. Zeit.*, 1914, **13**, 49.

<sup>7</sup> *Ibid.*, **14**, 35. Cf. his remark, "Die in der Arbeit *Koll. Zeit.*, **13**, 49, vertretene Ansicht, dass die Bildung der Peroxyde zur Depolymerization des hoch-polymerisierten ( $C_{10}H_{16}$ )—Moleküle führe, ist dahin zu berichtigen, dass der Peroxydbildung unbedingt eine Depolymerization vorausgehen muss."

He found that, owing to the more ready oxidizability of tannin as compared with caoutchouc, the admixture of 2-5 per cent. of tannin with *Hevea*, *Funtumia* or *Ficus* rubber during coagulation prevented, or greatly retarded, the onset of tackiness on exposing the rubber.

Gorter confirmed Fickendey's observations as to the non-occurrence of tackiness in an atmosphere of an indifferent gas. As already remarked, Gorter concluded that the oxidation of rubber was an autoxidation process. Examination of his tacky product showed that on distillation with water a dilute solution of an aldehyde was obtained which on boiling with ammonium acetate yielded pyrrole. The aldehyde was probably levulinic aldehyde. Some evidence was also obtained of the presence of levulinic acid. Gorter found a sample of *Hevea* sheet which was tacky in parts to give analytical figures indicating the presence of 2 per cent. of oxygen in the tacky part.

Henri<sup>1</sup> found the action of ultra-violet rays on rubber to bring about tackiness and oxidation. Bernstein<sup>2</sup> concluded that the primary effect of ultra-violet rays was to bring about a disaggregation ("depolymerization") of the caoutchouc, and that oxidation occurred as a secondary phenomenon, due to the ozone produced by the rays from atmospheric oxygen. Bernstein found the disaggregation (evidenced by a reduction of viscosity) of rubber in solution to be brought about by the rays of a quartz lamp in the absence of oxygen.

Whitby examined some exceptional samples of tree-scrap crêpe, encountered on a plantation, which were very badly tacky, and in which, it was found, a rapid oxidation of caoutchouc was proceeding. In the most severe case, the acetone-soluble portion of the rubber composed 26.8 per cent. of the material six weeks after the rubber had been harvested, and 78.02 per cent. six months later. At first the samples were tacky, but, as the oxidation proceeded, the samples lost their tackiness and acquired a shiny, smooth, dry surface. The viscosity of benzene solutions was, as is typically the case with tacky rubber, but little higher than the viscosity of benzene itself. The behaviour of these samples was similar to that of rubber undergoing oxidation under the catalytic influence of a copper salt.<sup>3</sup>

<sup>1</sup> *Le Caoutchouc*, 1910, 7, 4371.

<sup>2</sup> *Koll. Zeit.*, 1913, 12, 193.

<sup>3</sup> It was suggested at the time that the cause of the tackiness was probably organic (enzymic or fungoid). The evidence was not, however, sufficient to prove this suggestion; and, in view of the similarity in oxygen-content and in other ways of these samples to the products of the oxida-

*Tackiness in plantation rubber.*—As different conditions which may lead to tackiness in plantation rubber, the following may be mentioned<sup>1</sup>: (a) Exposure, in the air, to heat or sunlight<sup>2</sup>; (b) In the case of bark shavings and earth rubber, fermentative changes in the mass prior to cleansing; (c) Specific chemical agents.

Regarding (a): Whitby concluded that the first effect of sunlight was to produce disaggregation of the caoutchouc and tackiness; and that oxidation, and ultimately the replacement of tackiness by a dry, shiny appearance on the surface, followed. He found that, after three months' exposure to the sun, the acetone extract of a sample of crêpe, of which the original acetone extract was 2.63 per cent., had risen to 3.23, and after nine months' exposure to 8.33 per cent.

Regarding (b): Most of the tackiness encountered to-day in plantation rubber occurs in the two grades mentioned. Earth rubber, which appears on the market as a black or almost black crêpe, represents rubber which for various reasons has run on to the ground and coagulated there. Not infrequently the rubber is left on the ground for some considerable time before being collected, washed and crêped. This grade is tacky more frequently than any other. On a well-managed estate the grade represents only a very small fraction (say, one per cent.) of the total crop. In order to avoid tackiness in this grade, frequent collection and prompt cleansing are called for. A certain amount of rubber is present on the shavings of bark which are removed in the tapping operations. Bark shavings are preserved by the tappers, and by washing them on suitable rolls a grade of rubber known as bark crêpe is obtained. It is found that if large piles of bark shavings are left standing for a day or more, or often overnight only, the interior of the mass becomes quite hot, and this may lead to tackiness in the product. In order to avoid tackiness

---

tion of caoutchouc under the catalytic influence of copper, since investigated by him, the author is inclined to think it not impossible that the samples represented rubber which in some unrecognized manner had become contaminated with copper.

Certain tacky samples encountered by the author at a later date in all cases showed orange spots, which, it was thought possible, might have been due to a tackiness-producing fungus. An examination of the samples by A. Sharples failed, however, to reveal any active fungus.

<sup>1</sup> Whitby, *loc. cit.*

<sup>2</sup> Mention may be made here of a point of practice in this connection: If the exposure has been brief only (as, say, through direct sunlight falling accidentally on rubber in a drying shed), it is possible to remove the tackiness by re-crêping the rubber on wet rolls.

in bark crêpe, it is advisable to insist that bark shavings shall not be left more than one day before being worked up, and that they shall be kept in low piles only or under water.

Regarding (c) : Hydrochloric acid, when used in great excess as a coagulant, has been found to lead to tackiness.<sup>1</sup> The treatment of rubber with caustic alkalis frequently leads to tackiness. A number of metallic salts are capable of producing tackiness. The most potent of such salts are those of copper. It has occasionally been found that copper has been introduced during the preparation of raw rubber from brass machine bearings. It may also conceivably be introduced through the medium of the acetic acid used for coagulation. (It is usual to distil glacial acetic acid from copper stills.)

*Influence of salts of copper and other metals.*—The influence of copper in leading to the deterioration of rubber has long been recognized.<sup>2</sup> Extensive qualitative experiments on the influence of metals and metallic salts in producing deterioration of (cold-vulcanized) rubber were made by Thomson and Lewis.<sup>3</sup> The following are some of their conclusions : "Copper has a destructive effect far beyond that of any of the other metals." •The following had a comparatively slight injurious action : platinum, palladium, aluminium,<sup>4</sup> lead. Other metals had no effect. When saturated solutions of them were painted on the surface of rubber and the latter was heated at 140° F. for ten days, the following substances "entirely destroyed the rubber," namely: copper salts, arsenic iodide, silver nitrate, strontium nitrate, vanadium chlorate, red oxide of manganese, black oxide of manganese, bismuth chloride; the following "considerably damaged the elasticity of the rubber but did not entirely destroy it;" namely: ferrous nitrate, sodium nitrite, uranium nitrate, ammonium vanadate; the following "slightly damaged the elasticity of the rubber," namely: lead chromate, ferrous sulphate, zinc acetate,<sup>5</sup> zinc chloride, tin peroxide, tin perchloride, chromic acid, lead borate.

<sup>1</sup> Whitby, *Koll. Zeit.*, 1913, 12, 147.

<sup>2</sup> Cf. W. Thomson, *Chem. News*, 1890, 62, 192.

<sup>3</sup> *Mem. Manchester Lit. and Phil. Soc.*, 1891, 4 (4), 266.

<sup>4</sup> It may be mentioned that the employment of aluminium coagulating vessels (they have been used regularly for years on some estates) in the preparation of raw rubber has never been observed to lead to tackiness in the product.

<sup>5</sup> It may be mentioned that coagulation, by means of acetic acid, of latex in zinc vessels has not, in plantation experience, been found to lead to tackiness in the product.

The proportion of copper which is effective in producing deterioration of rubber is remarkably small. Eaton<sup>1</sup> found that raw rubber which had been immersed for one minute in a 1 per cent. copper sulphate solution and then washed for two hours in running water was already tacky after an interval of one week. Morgan<sup>2</sup> observed that the introduction of copper sulphate into latex prior to coagulation to the extent of 0.01 g. per 100 c.cs. led to tackiness and oxidation in the rubber prepared from such latex; an increase in weight of 7.7 per cent. being observed in a period of fourteen weeks. The present author in some quantitative experiments<sup>3</sup> confirmed the qualitative observation of Fox<sup>4</sup> that ammoniacal copper solutions were more active than copper solutions in producing tackiness. A sample of crêpe which had been immersed for twenty-four hours in a 0.5 per cent. ammoniacal solution of copper acetate and then washed and hung up in the air increased in weight during the first week by 1.43 per cent. During the same period the acetone extract rose from 3.5 to 11.9 per cent., and the relative viscosity in benzene solution fell from 25.75 to 2.05. Eaton<sup>5</sup> found iron salts to have an effect in producing tackiness noticeable but much less than the effect of copper salts.

*Disaggregation and oxidation.*—In regard to his experiments on the absorption of oxygen by raw rubber, Gorter interpreted the initial "lag" in the commencement of oxidation in the light of his general view of the process as an autoxidation. Whitby<sup>6</sup> pointed out that the lag could also be regarded as due to the necessity for a preliminary disaggregation (physical effect) of the caoutchouc before oxidation (chemical effect) could commence. Van Rossem<sup>7</sup> has made an experimental study of the question: "Does oxidation occur only when a certain degree of depolymerization or disaggregation has been obtained?" He showed first that it was possible to reproduce in a brief time (six hours) Fickendey's results, as to the occurrence of tackiness in an atmosphere of oxygen and its non-occurrence in an atmosphere of hydrogen, nitrogen or carbon dioxide, by working at a temperature of 130°. He therefore conducted his subsequent experiments at this temperature. He studied particularly solutions of *Hevea* rubber (of about 1 per cent. concentration, in

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 17, 1912, p. 27.

<sup>2</sup> "The preparation of plantation rubber," London, 1913, p. 164.

<sup>3</sup> Unpublished. With O. J. Walker.

<sup>4</sup> *J. Ind. Eng. Chem.*, 1917, 9, 1092.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Loc. cit.*

xylene), but later confirmed the principal results by experiments on solid rubber. The course of oxidation was followed by following the course of absorption of oxygen gas; two pairs of Hempel burettes being connected with the rubber-containing vessel. Samples could be removed for the purpose of viscosity determinations. It was found that oxidation never began until, after several hours' heating, the viscosity had fallen to a definite limit. This critical viscosity-limit was about 1.6-1.3 viscosity units for 1 per cent. solutions. It was found, further, that depolymerization (disaggregation) proceeded much more rapidly in an atmosphere of oxygen than in an atmosphere of carbon dioxide, even though the depolymerization in the presence of oxygen was not accompanied by absorption of oxygen.

It was concluded that (a) the oxidation, under the influence of heat, of rubber in solution or in the solid state is a secondary process, and is preceded by depolymerization; (b) the depolymerization of rubber by heat is catalytically accelerated by oxygen. The "acceleration of the depolymerization by oxygen as catalytic agent must be considered as the primary process causing tackiness of rubber."<sup>1</sup>

As already remarked, in the conclusions of van Rossem, the view that tackiness is primarily due to a reduction in the state of aggregation of caoutchouc, and the view that tackiness is dependent upon the presence of oxygen, are to a considerable extent reconciled. For, while the view that depolymerization or disaggregation is the fundamental cause of tackiness is maintained, it is also recognized that under ordinary circumstances the presence of oxygen is essential to tackiness, in that, apart from its catalytic influence on the depolymerization, under normal circumstances the latter would probably not take place appreciably in its absence.

Bernstein,<sup>2</sup> from a study of the effect of sulphur chloride on rubber solutions, concluded that vulcanization involved an initial disaggregation (depolymerization) followed by a great rise

<sup>1</sup> In relation to this conclusion the following experiment of Kirchhof (*Koll. Zeit.*, 1914, 14, 39) may be noted: A 3 per cent. solution of non-extracted Fine Hard Para was heated on the water bath at ca. 70°, and at intervals the fall in viscosity of the solution was determined. Another portion of the same solution was similarly heated, and during the heating a current of oxygen was passed through. The experiment was repeated with an extracted sample of Fine Hard Para. In neither case was it found that the passage of oxygen through the solution had any influence in accelerating the rate of reduction of the viscosity.

<sup>2</sup> *Koll. Zeit.*, 1912, 11, 185; 1913, 12, 273.

in the state of aggregation. He observed that both sulphur chloride and bromine—two substances which are pre-eminent among bodies capable of forming addition-products with caoutchouc—when added to rubber solutions, have the effect initially of reducing the viscosity of the solutions very rapidly. Bernstein remarked that “in the chemistry of caoutchouc it can often be ascertained that a depolymerization precedes reaction.” He remarked that, in addition to its reactions with sulphur chloride and with bromine, the oxidation of caoutchouc was favoured by light and heat, and that a depolymerized rubber was easily oxidizable.

Kirchhof<sup>1</sup> states, quite generally, that only after its depolymerization is caoutchouc capable of chemical action.<sup>2</sup> He supposes that the reason for the much greater depolymerizing effect of sulphur chloride or of bromine than of oxygen is due to its greater solubility. Other substances which have been found to have a depolymerizing effect on rubber in solution, as indicated by a fall in the viscosity, are potassium permanganate,<sup>3</sup> benzoyl peroxide,<sup>4</sup> *m*-dinitrobenzene.<sup>5</sup>

<sup>1</sup> *Koll. Zeit.*, 1914, **14**, 41.

<sup>2</sup> “Es musste auffallen, dass der Kautschuk, der in Lösungsmitteln Verbindungen gibt, welche unzweifelhaft auf die Anwesenheit zweier Doppelbindungen im Molekel schießen lassen, sich im festen Zustand mehr oder weniger passiv verhielt. . . . Erst nach erfolgter Depolymerisation ist der Kautschuk zu Additionsreaktionen befähigt und in Lösungen verhält er sich dann wie ein Molekel mit zwei Doppelbindungen, da hier die Depolymerisation quantitativ verläuft.” *Loc. cit.*

<sup>3</sup> Van Rossem, *Kolloidchem. Beihefte*, 1918, **10**, 1.

<sup>4</sup> Whitby and Walker (unpublished experiments).

<sup>5</sup> Bunschoten, *Chem. Weekblad*, 1918, **257**; *I.R.J.*, 1918, **56**, 719.



## CHAPTER IV

### THE PROTEIN

#### THE "INSOLUBLE" CONSTITUENT OF RUBBER

ALTHOUGH it had long been known that rubber-yielding latices contain protein,<sup>1</sup> only in 1907 was it definitely proved that the so-called "insoluble constituent" of Para rubber is largely composed of protein; although Gladstone and Hibbert had in 1888 justly assumed that such must be the case.<sup>2</sup>

When rubber is treated with the customary rubber solvents, such as benzene and chloroform, it first swells and then for the most part passes into (colloidal) solution. There always remains, however, an insoluble portion. The amount of the undissolved material is, as will appear in what follows, influenced considerably by the nature of any preliminary treatment of the rubber, the character of the solvent, the temperature, etc. The insoluble portion of raw rubber was commonly looked upon as an "insoluble modification" of rubber. Weber,<sup>3</sup> however, concluded that it was not a hydrocarbon, but corresponded on analysis to the formula  $C_{30}H_{68}O_{10}$ . He extracted an acetone-extracted sample of Fine Para with fresh quantities of chloroform until the solvent apparently ceased to extract any further appreciable quantity of soluble matter. The amount of "insoluble

<sup>1</sup> Cf., e. g., Faraday, *Quart. Jour. Sc.*, 1826, **21**, 19; Green, *Proc. Roy. Soc.*, 1886, **40**, 28.

<sup>2</sup> Weber's presentation (*J. Soc. Chem. Ind.*, 1900, **19**, 215) of Gladstone and Hibbert's conclusions on this point has passed into the literature, but appears to be based on a misreading of Gladstone and Hibbert's statement of their conclusions. A careful reading of their paper makes it appear that, in writing of the "less soluble modification of the hydrocarbon," they are not, as Weber assumes, writing of the "insoluble constituent" of rubber. That they recognized that the protein of latex must be included in the "insoluble constituent" is clear from their statement as follows: "It is well known that part of the caoutchouc of Para rubber is soluble in benzene and other solvents, and that a part is insoluble. Faraday also speaks of albumin as one of the constituents of the juice. We found the best solvent to be chloroform. This very slowly dissolves the whole of the hydrocarbon, leaving a sort of network of the nitrogenous body. In one experiment this residue was found to be about 4 per cent. of the whole weight."

<sup>3</sup> *J. Soc. Chem. Ind.*, 1900, **19**, 215.

constituent" which he thus obtained was 3.5 per cent. Weber failed to recognize the presence of nitrogen in his product. His formula is of historical interest only.

In 1907 Spence<sup>1</sup> studied the "insoluble constituent" of Para rubber, and showed it to contain an important quantity of protein. He treated raw wild Para rubber with successive, fresh quantities of chloroform,<sup>2</sup> and obtained samples of the insoluble constituent containing 1.74–5.4 per cent. of nitrogen. The product containing the last-mentioned amount of nitrogen was obtained as the result of a three-months' treatment with chloroform, the insoluble material being filtered off through muslin and treated with a fresh quantity of chloroform every week or so. The insoluble residue finally remaining in this case amounted to about 1 per cent. only of the original weight of rubber taken. If the customary factor for the conversion of nitrogen to protein, viz. 6.25, is used, the nitrogen-content of this sample indicated a protein-content of 33 per cent. Spence, however, thought it possible that the protein in question was a glyco-protein (nitrogen-content, *ca.* 10 per cent.). If such were assumed to be the case, and allowance were made for the ash of the insoluble material, its protein-content would come out as 60–70 per cent.

In the case of all these samples of the "insoluble constituent," extraction of caoutchouc was clearly incomplete. Some of the samples still showed many of the physical properties of rubber. The difficulty which the complete extraction of caoutchouc from the insoluble constituent presents is explicable in the light of microscopic observations which Spence made on the manner in which the protein is distributed throughout raw, wild Para rubber.

He found that the protein could be stained by the following procedure: soaking thin, hand-cut sections of the rubber in aqueous silver nitrate solution<sup>3</sup> for twenty-four hours, then

<sup>1</sup> *Quart. Jour. Inst. Comml. Res. in Tropics*, Liverpool, 1907.

<sup>2</sup> Chloroform was chosen as a much better solvent for the work than benzene on account of its greater rapidity of action in withdrawing the caoutchouc from its close association with the insoluble network.

The present writer found that, for the purpose of dissolving the caoutchouc out of samples of low-grade plantation crêpes, in order to decide from an examination of the insoluble matter as to the efficiency of the washing process, that chloroform was a much more suitable solvent than benzene.

<sup>3</sup> It is of interest to notice, in connection with the use of silver nitrate in staining the protein, that the addition of a small quantity of silver nitrate to the latex of *Hevea brasiliensis* has been found to have a striking effect (Whitby, *Koll. Zeit.*, 1913, 12, 154). When silver nitrate was added to latex, either in sufficient amount to produce coagulation or in small amount along with sufficient acetic acid to produce coagulation, the whole mass of coagulum became grey-coloured within a minute. If the grey coagulum

washing in running water for twelve hours, then soaking for twenty-four hours or more in a bath of tannic acid dissolved in 5 per cent. sodium carbonate solution, and, finally, washing well. According to Spence, in this way the silver salt deposited in the section is reduced to metallic silver. In order to secure a section of suitable thickness on the microscope slide, a hand-cut section is, following the procedure recommended by Ditmar, moistened for a short time with a drop of chloroform or carbon tetrachloride and is then squeezed out to the desired thickness by means of another slide screwed down on the top of the first by means of two screw clips. Spence found the protein to form a "peculiar thread-like or fibrous structure running throughout the entire mass of caoutchouc," reminding one "of the distribution of the fibrin in coagulated blood or of the elastic fibres of areolar tissue." The structure was shown even more clearly in acetone-extracted samples than in unextracted ones. Microphotographs of the structure are shown in the original paper. In only about one-third of several dozens of sections examined could the structure mentioned be detected by the staining method employed.

The mode of distribution of the protein, as a framework, in raw wild Para explains, in Spence's opinion, some of the peculiarities in the behaviour of the rubber towards solvents. The "protein," he says, "is distributed throughout the mass in the form of exceedingly delicate fibres or films, and such films would present an almost insurmountable barrier to the passage through them of the colloidal solution of the hydrocarbon. . . . The solvent passes through the walls of film of protein, and is slowly absorbed by the caoutchouc hydrocarbon, which becomes dilated thereby to a great extent, without being able to form part of the homogeneous colloid-solution. . . . The bulk of the insoluble product increases enormously, and a jelly-like mass is formed, which only slowly <sup>1</sup> disappears as the membrane gradually becomes imperfect

were kept away from air, no further discoloration took place; but, if it were exposed to air, or were washed and converted into crêpe, extraordinarily rapid darkening occurred, and within a few minutes the surface of the rubber was black. These effects of silver nitrate were attributed to a great accelerating influence on the activity of the oxidase of the latex. It is of interest to observe that Spence found in experiments on an African latex that the oxidase was associated with the protein of the latex. It is also of interest to note that Beadle and Stevens (*Koll. Zeit.*, 1912, **11**, 63) found that almost the whole of the material to which dark-coloured rubber owed its colour was present in the portion insoluble in benzene; being, they assumed, adsorbed by the insoluble constituent of the rubber.

<sup>1</sup> Caspari (*J. Soc. Chem. Ind.*, 1913, **32**, 1041) divides raw rubber into a soluble and a "pectous" portion; the latter portion being insoluble in cold petrol ether. In Caspari's view the proportion of the "pectous"

or breaks down completely." It is recognized that shaking increases the rate at which swollen rubber passes into solution. It is also well known that the "breaking down" of raw, wild Para on hot rolls brings the rubber into a condition such that it is much more readily soluble than before treatment and shows hardly any insoluble portion. The effect of the "breaking down" is presumably to disintegrate the fine network of protein; and the framework being no longer intact, a swollen "insoluble portion" is not apparent when the rubber is placed in a solvent.

In a solution prepared from such rubber the protein is for the most part or entirely distributed, in suspension, throughout the body of the solution in a finely-divided state; with the result that the solution appears comparatively homogeneous. Plantation sheet, in the preparation of which the coagulum is merely rolled, and plantation crêpe, in the preparation of which the coagulum is masticated, behave to solvents in a similar way respectively to unworked and to "broken down" Brazilian (*i. e.* wild) Para. That such is the case is shown by work of Beadle and Stevens<sup>1</sup> on the "insoluble portion" of plantation rubber. They state that plantation crêpe gave in benzene a solution (concentration not stated) which was apparently clear at the outset, but which on standing for several months deposited a precipitate, and, simultaneously, diminished notably in viscosity. After about twelve months' standing there was no further deposition, and no further change in viscosity. The precipitate which was thus deposited was found to contain only about 10 per cent. of the total nitrogen of the rubber. The rest of the nitrogen remained, presumably as protein in suspension, in the solution and could not be separated by fractional precipitation with alcohol or any other means employed. In the case of benzene solutions of plantation sheet, the insoluble portion, separable by filtration, contained almost all the nitrogen of the rubber; only about 10 per cent.

---

portion present in different samples of rubber bears a relation to the quality of the samples. This does not appear to be likely, as crêpe, according to Caspari, contains much less "pectous" rubber than sheet, and yet it gives, as will be noticed later, results very similar to those given by sheet on vulcanization. Stevens (*J. Soc. Chem. Ind.*, 1919, **38**, 194 T.) states that he has repeated Caspari's experiments, and was unable to obtain concordant results in repeat extractions. He found that the so-called pectous fraction, if allowed to stand sufficiently long with cold petroleum spirit, dissolved wholly, with the exception of a small quantity of slimy nitrogenous matter. He concludes that the behaviour of petroleum spirit as a solvent differs from that of benzene in degree, not in kind.

<sup>1</sup> *Koll. Zeit.*, 1912, **11**, 61.

remaining in the solution. In the case of unworked Fine Hard Para, about 50 per cent. remained in the solution.

The following table shows some of Beadle and Stevens' results. Nos. 1-3 represent different samples of pale crêpe; Nos. 4-7 different samples of smoked sheet; No. 8 a sample of smoked sheet, No. 9 the same after crêping; No. 10 Fine Hard Para; No. 11 a sample of crêpe treated with tannin. (The last sample is included here because of its interest in relation to the discussion, elsewhere, of the effect of tannin on latex.)

TABLE XXXII

No.	1	2	3	4	5	6	7	8	9	10	11
Nitrogen in original sample (per cent.)	0.45	.56	.41	.42	.42	.49	.48	.38	.38	.58	.47
Nitrogen in clear liquid after separation of insoluble portion	0.40	.41	.37	.04	.04	.03	.04	.05	.32	.23	.06

In their sample of the "insoluble portion" which had been most thoroughly washed—the washing having been repeated fifteen times over a period of four months—Beadle and Stevens found 7.0 per cent. of nitrogen and 4.8 per cent. of ash, as compared with corresponding figures of 5.4 and 8.4 in Spence's nitrogen-rich product from wild Para.

#### SEPARATION OF THE INSOLUBLE CONSTITUENT

What has already been said will have indicated that the colloidal character of rubber—the viscosity and other properties of its solutions—make a clean and complete separation of rubber into "soluble" and "insoluble" portions extremely difficult. Extraction with the customary rubber solvents at ordinary temperatures, even when continued for weeks or months, does not, as the results of Spence and of Beadle and Stevens show, suffice. In the methods more recently proposed for the separation of the insoluble portion of rubber, an essential feature is some means of so reducing the viscosity of the solution as to render the latter comparatively limpid. Tschirch and Schmitz<sup>1</sup> bring about the

<sup>1</sup> (*Gummi-Ztg.*, 1913, **26**, 2079.) 2.5 g. of thin, dried pieces of raw Para rubber are treated with 40-60 c.c. of pentachlorethane in a 500 c.c.-Erlenmeyer flask, and are heated at 80° in an oven until a limpid, homogeneous mixture is obtained (4-6 hours). After cooling, the liquid is diluted with a sufficient quantity (say, 400 c.c.s.) of chloroform, is filtered through an ordinary filter paper, washed with chloroform on the filter, or the carefully folded filter is extracted in a Soxhlet.

disintegration of the rubber by heating at 80° with pentachlorethane. Spence and Kratz<sup>1</sup> bring about a reduction in the viscosity of a benzene solution of rubber by means of a small proportion of an acid, preferably trichloroacetic acid. They attribute the effectiveness of pentachlorethane in Tschirch and Schmitz's method to acid present in ordinary samples of that reagent. In Dekker's<sup>2</sup> procedure, dissolution of the rubber and separation of the insoluble are brought about by heating at 230–260° in petroleum of that boiling point.

Tschirch and Stevens state that the separation of the rubber protein was almost complete by their method. Thus, from a sample of raw Para rubber containing 0.3571 per cent. of nitrogen, an insoluble portion was separated which contained 0.345 per cent. nitrogen (calculated on the original rubber). The insoluble

<sup>1</sup> *Koll. Zeit.*, 1914, 14, 262. For the separation of a considerable quantity of the insoluble portion for the purpose of chemical examination, the following procedure was employed: 100 g. of washed and dried rubber are put into one litre of benzene containing 0.3–0.5 per cent. of trichloroacetic acid. If the rubber has been previously worked on the rolls, it goes into solution more rapidly than otherwise. The solution is placed if possible in sunlight or is warmed on the water-bath. As a rule, after twenty-four hours in sunlight, with repeated, strong shaking, complete solution and disintegration of the rubber has occurred. The fine particles of insoluble material agglomerate and fall to the bottom. (Do not shake violently at this stage.) For the purpose of obtaining a sample of the insoluble matter for examination, the upper liquid can be decanted and the insoluble residue washed by two successive treatments of several hours with a further quantity (500 c.cs.) of acid-containing solvent. Filter; wash with benzene; powder in a mortar; wash with further solvent until no more traces of caoutchouc are extracted; wash with alcohol; dry. For the purpose of securing a quantitative separation, it is recommended to use centrifugation and filtration. In such case it is better to make the original solution 2 per cent. instead of 10 per cent.

It may be mentioned, as a point of interest, that the depolymerized rubber, which, as recovered by evaporation of the benzene solution according to the above procedure, is of a syrupy consistency, can, Spence and Kratz state, be converted into a tough, elastic product, soluble with difficulty in rubber solvents, by treatment with sodium or alkali derivatives. (Cf. *Eng. Pat.*, 1912, No. 17,667.) The effect of sodium on the viscosity of rubber is, it will be observed, opposite to that of acids, bromine, etc. The remarkable polymerizing effect of sodium on rubber of low viscosity is confirmed by Esch (*Rubber Industry*, 1914, p. 152) and by Martin (*ibid.*, p. 153).

<sup>2</sup> *Meded. Delft*, 1916, p. 483; *Delft Communics.*, pp. 56 et seq., 2 g. of rubber are heated with 40 c.cs. of the petroleum fraction 230–260° in a small flask provided with an air condenser for three hours. With unmasticated rubber (as, e.g., sheet) the insoluble matter separates as flakes. With crêpe, separation has not occurred after three hours' boiling; and in such cases 20 c.cs. further of the petroleum is added and the boiling is continued. After cooling, the liquid is diluted with an equal volume of benzene and is filtered through asbestos on a Gooch crucible. The contents of the crucible are washed out with about 50 c.cs. of benzene, and are dried to constant weight at 105°.

portion from sample of Para was 2.9-3.1 per cent. and contained 11-12.6 per cent. of nitrogen. After subtracting the ash of the insoluble portion, its nitrogen-content appeared as 14-15.6 per cent. Schmitz<sup>1</sup> made a subsequent communication on results obtained by the use of this method. He states that the nitrogen-content of samples of insoluble material separated was 13.8-16 per cent. In view of these figures, he concludes that it is not necessary to assume, as Spence had supposed, that the rubber proteins differ from simple plant proteins. The samples of insoluble material isolated by the use of pentachlorethane consisted of dark, dry, amorphous powders, which, when wetted with chloroform, did not swell, and which did not show any of the other peculiarities of the caoutchouc hydrocarbon. They were soluble in 5 per cent. sodium hydroxide solution, with the exception of a small residue, chiefly inorganic in character. It should be noted, however, that unambiguous protein reactions could not be obtained with the solutions.

Spence and Kratz<sup>2</sup> passed some criticisms on Schmitz's communication. On applying Schmitz's method to their own rubber samples, they obtained nitrogen-values in agreement with those obtained according to their own process (see p. 116), and not in agreement with the values given by Schmitz. They remark that Schmitz's analyses are made on the insoluble constituent from only 2.5 g. of rubber, and that, on account of this, the experimental error may be considerable.<sup>3</sup> Further: they cannot agree

<sup>1</sup> *Gummi-Ztg.*, 27, 1085, 1131. Also, *Ibid.*, 28, 1740.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Determination of Nitrogen in Rubber by Kjeldahl's Method.*—A note may be made here on the determination of nitrogen in rubber after Kjeldahl. Schmitz had earlier (*Gummi-Ztg.*, 1913, 26, 1877) recommended a modification of the ordinary Kjeldahl procedure, which, he claimed, was more delicate than the latter. The ammonia is drawn out of the liquid by means of air (Cf. Classen, Folin and others) into acid, the excess of which is determined by treatment with potassium iodate and potassium iodide followed by titration with thiosulphate.

The procedure given by the Delft Institute for the application of the Kjeldahl method to rubber is as follows: Place 1 g. of the finely cut sample in a digestion flask; add 1 drop of mercury and 30 c.c.s. of phosphoric-sulphuric acid (1 litre concentrated sulphuric acid, 200 g. phosphorus pentoxide). When the rubber has been entirely impregnated with the acid, start heating with a small flame; and, when foaming diminishes, increase the flame gradually, until the liquid boils. Continue boiling for a short time after the liquid has become colourless. Proceed as usual.

Owing to the high carbon-content of caoutchouc, the complete oxidation of the carbonaceous matter from a rubber sample which is undergoing digestion usually demands a rather prolonged period of digestion. Howie (*J. Soc. Chem. Ind.*, 1918, 37, 88 T), however, states that it is not necessary to continue the digestion until the liquid is colourless. He found that complete conversion of the nitrogen into ammonium sulphate had occurred in about half the time that was necessary to consume all the suspended

with Schmitz that it is legitimate to deduct the total ash-content of the products before calculating their nitrogen-content.

Spence and Kratz investigated the insoluble constituent isolated from Fine Hard Para and from plantation rubber by their method, already mentioned, involving depolymerization of caoutchouc through the agency of heat and an acid. It was, they state, absolutely free from adhering caoutchouc, as shown by its solubility in alkali. It had on the average a nitrogen-content of 10.3 per cent., and it gave the characteristic reactions for protein and for carbohydrate.<sup>1</sup> They concluded that the protein of *Hevea* rubber is not a simple vegetable protein, but probably a glycoprotein, and that, in consequence, not the ordinary factor, 6.25, but possibly a factor of about 10 should be employed in calculating rubber protein from results for nitrogen. Spence<sup>2</sup> had earlier concluded that the protein of *Funtumia elastica* latex gave not only protein, but also sugar reactions.

Prior to the development of their own method for the isolation of the insoluble constituent, Spence and Kratz investigated the ability of a number of other proposed methods to give pure, nitrogen-free caoutchouc hydrocarbon. Their conclusions in this connection were as follows:—

(a) The methods, involving precipitation from solution, which have generally been employed by earlier workers for the preparation of pure caoutchouc, fail to allow for the characteristic properties of colloidal rubber solutions. The precipitated caoutchouc carries down (in an adsorbed condition) protein. The method of Harries,<sup>3</sup> for example, in which the rubber is put three times through the procedure of extraction with alcohol, dissolution in benzene, and precipitation with alcohol, when applied to a Para rubber sample containing originally 0.17 per cent. of nitrogen, gave a product which still contained 0.13 per cent. of nitrogen.<sup>4</sup>

(b) A successful separation of the soluble and insoluble parts could not be obtained by any of the ordinary neutral solvents.

---

carbon. Treating 1 g. of plantation sheet with 30 c.cs. of sulphuric acid, 7 g. of potassium sulphate, and 1 g. of anhydrous copper sulphate, he found that, while six hours' digestion was required to produce a transparent, although not colourless, liquid, after 3–4 hours' digestion distillation could be proceeded with and all the nitrogen determined.

<sup>1</sup> Spence and Kratz remark that the "insoluble" of wild Para (Fine Hard Para) gave positive reactions for protein and for sugar only with extraordinary difficulty. It gave them only after being dissolved in dilute alkali (cf. p. 117).

<sup>2</sup> *Biochem. Jour.*, 1908, **3**, 175.

<sup>3</sup> *Ber.*, 1905, **38**, 1198.

<sup>4</sup> Spence and Galletly, *Techn. Monatsh.*, 1911, **5**, 111.



(c) A complete separation could not be secured in the case of wild Para or plantation rubber by means of the sedimentation or centrifugation of even dilute solutions; although under carefully determined conditions an almost complete separation was possible in the case of Manicoba rubber. (d) Treatment with boiling toluene did not produce complete separation. Treatment of 5 g. of Manicoba rubber with 400 c.cs. of boiling toluene for  $4 \times 10$  hours, followed by treatment for  $12 \times 10$  hours with fresh toluene daily, gave an insoluble portion containing in two samples respectively 7.36 and 6.40 per cent. of nitrogen, 9.9 and 18.8 per cent. of ash.

(e) Digestion of plantation rubber with 1-10 per cent. hydrochloric acid for forty-eight hours in the cold, and forty-eight hours under reflux, reduced the nitrogen-content only from 0.343 to 0.257 per cent. (f) Digestion of plantation rubber for several days in the cold, and finally at boiling temperature with 5 per cent. aqueous potassium hydroxide, reduced the nitrogen-content from 0.2180 to 0.1658 per cent., and with 5 per cent. alcoholic potassium hydroxide from 0.2180 to 0.0545. (g) The action of alcoholic alkali was favoured somewhat by swelling the rubber in a rubber solvent. By conducting the digestion of plantation rubber with a mixture of one volume of naphtha and two volumes of 5 per cent. alcoholic sodium hydroxide, the nitrogen-content, after two treatments, had been reduced from 0.296 to 0.041 per cent. By the procedures (e)-(g), naturally, the protein cannot be isolated; and, further, the rubber obtained by the use of alkali quickly deteriorates.

By the application of their trichloroacetic acid method of isolating the protein, Spence and Kratz obtained the following results:—

Samples of the insoluble constituent were prepared from plantation rubber. A product obtained by the method mentioned showed, after being extracted once with a fresh quantity of solvent, a nitrogen-content of 9.83 per cent. The product was then extracted, several times in succession, in sunlight, with benzene (shaking occasionally) for several hours; it was then boiled with benzene under reflux for five hours, and was then washed and dried. After this treatment it had a nitrogen content of 12.08 per cent. and gave only 2.06 per cent. ash. (Sample No. 2). This sample showed the maximum nitrogen-content obtained. Its nitrogen-content was not increased by treating it, according to Schmitz's procedure, for six hours at  $90^\circ$  with pentachlorethane.

The nitrogen-content of the product recovered after treatment according to the last-mentioned procedure was 11.58 per cent. Sample No. 2 was dissolved by gentle warming in a 1 per cent. solution of sodium hydroxide, and was reprecipitated by acetic acid. The precipitate contained 10.9 per cent. of nitrogen.

*Reactions and chemical character of the insoluble constituent.*— Each of the four products mentioned above showed the following reactions: Easily soluble on gentle warming in 1 per cent. sodium hydroxide solution; insoluble in 2 per cent. sodium carbonate solution, in water and in dilute acid. Precipitated by acetic acid, hydrochloric acid, tannic acid (from neutral solution), ferrocyanide-acetic acid mixture. Precipitated slowly by alcohol. Positive results in the Xanthoproteic, the Heller, the biuret, Millon's, the Adamkiewicz, the Liebermann and the Molisch reaction. Reduction of Barreswil's (Fehling's) solution after hydrolysis, or, directly, in alkaline solution. Gave the Molisch reaction after hydrolysis with 20 per cent. sulphuric acid. Gave the phloroglucin-hydrochloric acid reaction for pentoses.

Spence and Kratz concluded that the protein of plantation rubber has undoubtedly the character of a glycoprotein (glucoprotein). They remark that its reactions are the reactions which are characteristic of mucins. They did not, however, isolate glycuronic acid or an amino sugar from it.

Spence and Kratz encountered more difficulty in dealing with the protein of Fine Hard Para than in dealing with that of plantation rubber. The highest percentage of nitrogen found in any of the products isolated from Fine Hard Para was 10.5. The product dissolved completely in warm alkali solution and was thrown out on acidification. But, in contrast with the products from plantation rubber, it gave *directly* none of the characteristic reactions for protein or for carbohydrates, with the exception of the xanthoproteic reaction. (The latter is not regarded as being strictly characteristic.) Not even after long hydrolysis with 20 per cent. sulphuric acid could a reaction be obtained for carbohydrate. The product was, in short, extraordinarily stable and indifferent towards reagents. In the case of the sample, mentioned above, containing 10.5 per cent. of nitrogen, which had been dissolved in alkali and thrown out by acid, positive results for Millon's and for the Molisch reactions could, however, be obtained with the resulting mother liquor. Spence and Kratz concluded that, despite this difference in behaviour, the results on the whole showed that the protein of Fine Hard Para

is similar to the protein of plantation rubber, and that, at all events, the protein of Fine Hard Para has not the character of a simple protein.

Frank<sup>1</sup> employed, for the purpose of dissolving the caoutchouc and isolating the protein, boiling cymene, limonene or dipentene. His method is as follows: 1-2 g. of raw rubber is heated with 30 c.c.s. of one of the above-mentioned solvents at the boiling temperature of the solvent until a thin solution is obtained. The solution is centrifugated at 2500-3000 r.p.m. for 1-1.5 hours. The residue is treated successively with xylene, benzene and ether; it is then dried. Frank states that results obtained by different experimenters with this method did not as a rule differ by more than 0.1 per cent. He does not, however, give any fuller data on the point. The protein as isolated by this method gave the biuret reaction clearly; it gave positive results with the xanthoproteic, the lead sulphide, and Millon's reactions. (Tyrosin was later identified with certainty in most of the products.) Liebermann's reaction gave uncertain results. It gave all the precipitation reactions of proteins. The products obtained by the hydrolysis of the comparatively small quantity of material available agreed, Frank states, so far as they could be observed, with the products "found in caoutchouc latex and in the serum after coagulation."<sup>2</sup> After hydrolysis with sulphuric acid, there was identified with certainty monoaminocarboxylic acids, aromatic amino acids (phenylalanine and tyrosin), heterocyclic amino acids (tryptophane for certain), diamino acids, and, with fair certainty, monoaminodicarboxylic acids and cystine. The presence of amino acids in the products, particularly when they showed slight signs of disintegration, could be shown by means of ninhydrin.

Dekker<sup>3</sup> tested a number of the procedures which have been suggested for the determination of the "insoluble" in raw rubber. He concluded that all the procedures examined were untrustworthy<sup>4</sup> and developed, in their stead, the method, involving

<sup>1</sup> *Rubber Industry*, 1914, p. 144.

<sup>2</sup> For some observations on the character of the breakdown products, derived (by putrefaction) from the proteins of latex serum, vide Whitby *Koll. Zeit.*, 1913, 12, 147.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> The methods tested were as follows: Spence's early method, using xylene at 100°; Dittmar's modification of Spence's method (*Die Analyse des Kautschuks*, Wien u. Leipzig, 1909, p. 157); Tschirch and Schmitz's pentachlorethane method (*loc. cit.*); the use of xylene at 135°; solution, with shaking, in xylene; Marquis and Heim's method (*Bull. Soc. Chim.*, 1913, 13 (4), 362), employing sulphuric acid, added to a chloroform solution.

heating at 230–260° in petroleum, already mentioned. He studied the results given by this method. Following Beadle and Stevens,<sup>1</sup> Dekker regards the difficulty which the separation of the insoluble constituent from rubber presents as arising from the protective action of the rubber colloid. The following table indicates the character of some of the results obtained by Dekker when applying his method. In the case of each sample the effect of the heating was followed by determining the amount of the insoluble material which had separated, and the viscosity of the liquid at a number (mostly 7–9) of intervals up to a period of twelve hours. Row (b) shows the period of heating required to bring the action to a conclusion: further heating, beyond this period, brought about practically no further separation of insoluble. Rows (c–e) show the condition of affairs after the period of heating given in row (b). Rows (f) and (g) refer to the insoluble material as separated by the longest period of heating in question in each case, *i. e.* twelve hours.

TABLE XXXIII

	Fine Hard Para (untreated).	Fine Hard Para (washed).	Planta- tion crêpe.	Planta- tion sheet.
(a) Protein in original rubber (per cent.) . .	2.40	2.24	2.43	3.10
(b) Period of heating for completion of action (hrs.)	<i>ca.</i> 6	2	3	0.25
(c) Percentage insoluble	2.75	3.30	2.69	3.03
(d) Protein in insoluble { After	1.44	1.57	1.64	1.70
(e) Relative viscosity of solution { period of	2.54	4.12	3.79	9.68
(f) Percentage of nitrogen in original rubber				
recovered in the insoluble . . .	55	—	65	55
(g) Percentage of nitrogen in insoluble . . .	8.5	—	11.0	9.2

It will be observed that only 55–65 per cent. of the total “nitrogen calculated as protein” is recovered in the insoluble fraction. As already mentioned in the preceding chapter, Dekker found that some of the nitrogen in rubber was soluble in acetone. The amount thus soluble would not, however, appear to be sufficient to account for the whole of the nitrogen unrecovered by the above procedure.

It is of interest to observe that the percentages of nitrogen found by Dekker in the insoluble portion are of the same order as those found by Spence and Kratz. In addition to the figures given in row (g) of the above table, Dekker gives figures for other samples as follows: A sample of Fine Hard Para, 9.9; another sample of plantation crêpe, 11.0.

<sup>1</sup> *Koll. Zeit.*, 1912, 11, 61.

It is of interest to observe that the separation of the insoluble matter from plantation sheet occurs more readily—after only a short period of heating, and before the viscosity of the liquid has fallen far—than from plantation crêpe. This is in agreement with the observations of Beadle and Stevens as to the relative ease with which the insoluble is separated from the two forms (p. 111).

Dekker compared, for eighteen samples of plantation rubber, the figure obtained indirectly for the caoutchouc-content by two methods, viz. (A) subtraction from 100 per cent. of the percentages found separately for moisture, resin, ash and protein (factor, 6.25); (B) subtraction from 100 per cent. of the percentages found separately for moisture, resin and insoluble (according to Dekker's method). B invariably gave a higher figure than A. This would be expected in view of the previous conclusion that only 55–65 per cent. of the protein appeared in the insoluble portion. But the differences between the results according to A and those according to B were not excessively great. They ranged from 0.21 to 0.75 per cent.

#### INFLUENCE OF THE INSOLUBLE CONSTITUENTS ON VULCANIZATION

It was shown by Beadle and Stevens<sup>1</sup> that the insoluble matter present in normal samples of *Hevea* rubber<sup>2</sup> plays an important rôle in the vulcanization of such rubber. By treating a sample of smoked sheet with benzene, they prepared from it a sample (No. 4) poor in nitrogen and a sample (No. 3) rich in nitrogen. The former sample was derived from the upper part of the solution obtained by pouring benzene on the sheet; the latter from the lower part of the solution, where the insoluble matter was concentrated. The former was of a pale colour and contained only a little of the insoluble constituent; the latter was of a dark colour and contained most of the insoluble constituent. In addition to the above samples, a sample (No. 2) of the same sheet was merely swollen in benzene, the benzene being allowed to evaporate off. This sample was included in order to determine whether the swelling itself influenced the results. A sample (No. 1) of the original,

<sup>1</sup> *Koll. Zeit.*, 1912, 11, 61.

<sup>2</sup> Beadle and Stevens (*Koll. Zeit.*, 1913, 12, 46) found a similar marked effect of the insoluble on vulcanization in the case of Rambong (*Ficus elastica*) rubber. They also found a similar effect, within the limits of their experiments less marked, in the case of Ceara rubber.

untreated sheet was also examined. The samples were all vulcanized under the same conditions.<sup>1</sup> After vulcanization they were tested on the Schwartz machine.<sup>2</sup> The results obtained are shown in the following table.

TABLE XXXIV

Sample No.	1	2	3	4
Nitrogen in sample (per cent.)	0·48	0·48	0·80	0·25
Cured for 3 hrs. at a pressure of 2·10 kg./cm <sup>2</sup> .				
Combined sulphur (per cent.)	2·68	2·80	3·30	0·55
Extension under 200 g./mm. <sup>2</sup> First cycle (per cent.)	321·6	322·4	291·2	470·4
" " Fifth " (" " )	487·2	481·6	417·6	656·0
Cyclic remainder (per cent.)	46·8	46·0	37·6	125·6
Cured for 3 hrs. at a pressure of 2·46 kg./cm <sup>2</sup> .				
Combined sulphur (per cent.)	3·76	3·77	4·21	2·46
Extension under 200 g./mm. <sup>2</sup> First cycle (per cent.)	303·2	309·2	305·2	452·4
" " Fifth " (" " )	429·2	440·0	401·6	716·0
Cyclic remainder (per cent.)	30·4	32·8	26·4	77·2

It is clear from these results that the nitrogen-rich sample vulcanized more rapidly and the nitrogen-poor sample much more slowly than the normal samples. The swelling in benzene itself proves to have no appreciable influence on the vulcanization results. The above result as to the importance of the insoluble matter in the vulcanization process was confirmed by a further series of experiments.<sup>3</sup> In the series of samples examined in these further experiments the nitrogen-poor sample contained only 0.070 per cent. of nitrogen. When vulcanized, in a mix containing 7 per cent. of sulphur, for three hours at 45 lb. steam pressure, this sample combined only with 0.8 per cent. of sulphur.<sup>4</sup>

Stevens <sup>5</sup> has investigated the influence of additions of various substances on the vulcanization of smoked sheet from which, by means of benzene, in the manner indicated above, the greater part of the insoluble material had been removed. His results are shown in the following table. The samples were vulcanized with

<sup>1</sup> Apparently the mix consisted of 100 rubber: 5 sulphur.

<sup>2</sup> Cf. p. 417; also Beadle and Stevens, *J. Soc. Chem. Ind.*, 1911, 1421.

<sup>3</sup> Beadle and Stevens, *J. Soc. Chem. Ind.*, 1912, **31**, 1099.

<sup>4</sup> Spence and Young (*Koll. Zeit.*, 1913, **13**, 265) give some rather striking data showing the rate of combination of sulphur with rubber, of progressively increasing degrees of "purity," vulcanized for periods of 5 mins. to 20 hours. The greater the degree of purity of the rubber, the more slowly did sulphur enter into combination. The authors do not, however, give any information as to the character of the impurity or impurities with reference to which the series shows progression or as to the method by which the samples were prepared. The same authors (*ibid.*) found that samples of balata free from insoluble nitrogen or other admixture combined with sulphur as quickly as corresponding samples free only from acetone-soluble admixture.

<sup>5</sup> *Koll. Zeit.*, 1914, **14**, 91.

7 per cent. of sulphur for three hours (temperature of vulcanization not stated). In the case of No. 4, the peptone was mixed with the nitrogen-poor rubber on the mixing mill; in the case of No. 5, it was added, in the form of an aqueous solution, to the benzene solution of the rubber; the mixed solution being emulsified and evaporated. In the case of No. 6, casein, dissolved in the smallest possible quantity of ammonia, was added to the benzene solution. The starch in No. 7 was added on the mixing rolls.

TABLE XXXV

Sample No.		P <sub>500</sub> .	Sub-permanent set immediately after five extensions under a max. load of 200 g./mm. <sup>2</sup>	Vulcn. coeff. (on the resin- and protein-free rubber).
1	Original rubber . . . . .	0.178	25.6	2.86
2	Rubber with excess of the insoluble matter . . . . .	0.267	12.4	3.62
3	Rubber "free" from insoluble matter . . . . .	0.055	Broke	1.15
4	No. 3 with 3 % peptone (Riedel) . . . . .	0.165	20.0	3.22
5	" " " " (added in solution) . . . . .	0.166	23.6	2.89
6	" " " casein . . . . .	0.106	57.2	1.76
7	" " " starch . . . . .	0.073	Broke	1.46
8	" " " 10 % litharge . . . . .	0.308	8.8	3.02
9	" " cured for 8 instead of 3 hrs. . . . .	0.158	24.0	2.16

A comparison of the results for Nos. 1, 2 and 3 confirms the previous conclusions of Beadle and Stevens as to the importance of the insoluble matter in vulcanization. It may be said, broadly, that the lower the figure for P<sub>500</sub> (indicating the resistance to extension), the lower the figure for the sub-permanent set, and the higher the figure for the vulcanization coefficient, the more advanced is the state of cure. No. 3 is much under-cured.

Starch, which is presumably an indifferent substance in regard to the reaction between sulphur and caoutchouc, is seen to have little effect on the vulcanization. Peptone, and, to a smaller degree, casein<sup>1</sup> appear, however, to be capable of performing the same function in vulcanization as that normally performed by the insoluble matter of the rubber. A typical inorganic catalyst of vulcanization, viz. litharge, is also seen to be capable of replacing the insoluble matter as an accelerator of vulcanization. That the effect of the absence of the insoluble matter is essentially to reduce the rate of vulcanization, appears from the fact that, when, as in No. 9, the sample which has been deprived of its insoluble matter is

<sup>1</sup> Esch (*Rubber Industry*, 1914, p. 134) states that glue gives the same results as casein.

cured for a longer period, it gives results approximating to those given by the original, untreated rubber. Eaton<sup>1</sup> found that the addition of casein or of peptone to the extent of 4 per cent. to a mix of 90 crêpe rubber : 10 sulphur had only a slight influence on the rate of cure, as judged by tensile properties. The rubber in this case had not, however, as it had in Stevens' experiments, been deprived of its insoluble matter.

Van Rossem<sup>2</sup> calculated the coefficient of correlation of the nitrogen-content and the vulcanization coefficient (indicating the rate of cure) in collections of samples cured under the same conditions, and found it to have a slight negative value. For a collection of 101 latex crêpes, it was  $-0.029 \pm 0.067$ ; for a collection of the same 101 crêpes together with 33 sheets, it was  $-0.054 \pm 0.058$ . The investigations of Eaton and Grantham into the relation between the nitrogen-content of rubber and its rate of cure, have shown that in the rapid-curing type of rubber obtained by maturation of the wet coagulum the nitrogen-content is characteristically lower than the nitrogen-content of slower-curing rubber obtained by crêping the coagulum shortly after its preparation. A similar result is given by experiments in Ceylon. The fact that, despite the important accelerating influence of the insoluble (nitrogenous) portion of rubber on the rapidity of vulcanization, which Stevens' experiments demonstrate, there should not be a positive correlation between the nitrogen-content and the rate of vulcanization of rubber samples is explained by the circumstance that there are present in rubber, particularly when bacterial disintegration of a part of the protein has occurred, small quantities of nitrogenous substances which are much more active in promoting vulcanization than the insoluble or nitrogenous matter considered as a whole. This aspect of the relation of the nitrogenous constituents of rubber to its rate of vulcanization will be fully discussed in the chapter on Maturation of the Coagulum.

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 84 *et seq.* Also Eaton and Grantham, *J. Soc. Chem. Ind.*, 1916.

<sup>2</sup> *Bijdrage tot de kennis van het vulcanisatieproces*, Amsterdam, 1916, p. 128.



## CHAPTER V

### COLLECTION OF LATEX—COAGULATION IN THE FACTORY

AFTER the trees have been tapped and have ceased to drip, the latex in the cups is collected in pails, and is taken to a central point, either the estate factory or a sectional station. At this point it is coagulated. It is not possible to secure in the uncoagulated, liquid condition quite all the latex which issues from the tree. The latex remaining on the cuts, vertical channels and spouts when the trees have ceased to drip, dries in position. The proportion of such latex varies, of course, with the yield of the trees, but as a rule is rather less than 10 per cent. of the total. So far as it is possible or practicable, the ribbons of rubber which have dried on the cuts and elsewhere are stripped off next morning just before the tree is tapped. The rubber so obtained is termed "tree scrap." It is, later, washed and crêped, the product being termed "scrap crêpe."

Such dried latex as is not stripped off the cuts is naturally to be found mostly on the parings of bark removed in tapping. The parings, known as "bark shavings," are preserved by the tappers. Later, the rubber on them is obtained by washing and milling, and, finally, crêping; the product being known as "bark crêpe."

In addition to the latex which dries on the tree, a further small quantity fails to find its way into the cups, but, instead, drips on to the ground, owing to a variety of accidental circumstances, such as failure to run down the prescribed channel, carelessness of the tapper in placing the cup under the tree, the abnormal issue of latex due to attacks by white ants. Such latex coagulates on the ground. At intervals the ground at the base of the tree is examined, and such rubber as may be found is collected. The rubber thus collected is known as "earth rubber." After washing and milling it is converted into "earth crêpe," which is usually black. Only a comparatively insignificant amount of the latex goes to form earth crêpe, its amount

on a well-managed estate being not more than, say, 1 per cent.<sup>1</sup> of the crop.

Of the latex which collects in the cups, a small proportion undergoes natural coagulation during the interval of, say, four to five hours between the tapping of the trees and the delivery of the latex at the coagulating station. Such natural coagulum is known as "lump" or "lump scrap." It is washed and converted into "lump crêpe." The proportion of lump crêpe in the crop varies considerably with the circumstances of the estate. It has never been found possible entirely to avoid the formation of lump. As high a proportion of lump crêpe in the crop as 10 per cent. is by no means unknown; but, unless the circumstances on an estate are exceptionally adverse in this regard, it is usually possible by good management to keep the proportion of lump down to 2-4 per cent. of the crop.

The following table shows the different grades into which a plantation's crop is divided, together with their proportions under reasonably favourable circumstances on well-managed plantations. The proportions, however, vary a good deal; those given are only approximate. The order of the grades in the table represents their order of relative quality, as judged by the market price, and broadly—so far as our data go—as judged by their behaviour on vulcanization.

TABLE XXXVI

Grade No. 1.	Latex rubber	.	.	.	86-88 per cent.
" " 2.	Lump crêpe	.	.	.	2-4 " "
" " 3.	Scrap crêpe	.	.	.	} 9 " "
" " 4.	Bark crêpe	.	.	.	
" " 5.	Earth crêpe	.	.	.	

The term "lower grades" may be taken generally as indicating grades Nos. 2-5, and the term "low grades" as indicating grades Nos. 3-5.

*Formation of lump.*—Lump forms both while the latex is in the cups and after it has been collected in the pails. Some of the factors which influence the proportion of lump formed may be mentioned: (a) The latex from occasional, individual trees shows persistently a tendency to exceptionally rapid natural coagulation.<sup>2</sup> (b) The tapping conditions may exert consider-

<sup>1</sup> A low figure for earth rubber in estate returns may, of course, be due, not to care in avoiding the formation of, but to negligence in collecting earth rubber.

<sup>2</sup> Cf. Whitby, *Ann. Bot.*, 1919, **31**, 321.

able influence on the readiness with which lump forms. The author found that, in general, the higher a cut is situated on the trunk, the greater is the likelihood of rapid coagulation taking place in the latex issuing from it. Hence, it is a fundamental, practical consideration, not only, as already mentioned, in devising a tapping system which shall yield the largest feasible amount of rubber, but also in securing the largest possible proportion of grade No. 1 in the crop, that the cuts shall all the time be kept at as low a level as possible on the trunk. (c) The opening up of new cuts during periods of dry weather increases the proportion of lump. (d) Agitation of the latex, as during its transportation, favours the production of lump. (e) All delay in tapping the trees, in collecting the latex and in transporting the latex to the coagulating station is, naturally, favourable to the onset of natural coagulation, and thus to a high proportion of lump. The avoidance of delay in these respects is, of course, a question of estate management. Speaking generally, it represents the first matter for consideration in keeping the proportion of lump in the crop down to a minimal figure.

Where the circumstances of an estate are such that the undue occurrence of natural coagulation cannot be avoided by other means, an anti-coagulant can be added to the latex.

The avoidance of natural coagulation is of importance, not only in order that the proportion of lump in the crop may be minimized, but also because of numerous difficulties which a condition in the latex of incipient natural clotting—a condition of “thickening”—places in the way of the preparation of sheet acceptable to the market (cf. section on Bubbles in Sheet, Chapter VII).

*Collection of latex.*—There are certain differences in the practice of different estates in regard to the employment of water in the collection of latex. Some years ago it was the custom to place a little water in the collecting cups before putting them under the just-tapped trees; but it was found that this not infrequently led to the undue dilution of the latex, and did not reduce the percentage of lump below the figure which could be obtained without such an introduction of water. Hence, the introduction of water into the cups was generally abandoned; although its use, in collecting, for washing out latex remaining in the cups after the greater part has been poured into the collecting pails was generally continued. Recently a good many

estates have abandoned the use of water altogether, and have adopted so-called dry-tapping. According to this procedure, what latex remains on the sides of the cup after as much as possible of the (viscous) latex has been poured into the pail is allowed to dry in the cup and is pulled off later in the day or on the following day. This procedure gives undiluted latex.

Instead of the residuum of latex in the cup being, as in the above procedure, left to dry, it may be washed out with water. If it is desired to employ undiluted latex for the preparation of the rubber at the coagulation station, the much-diluted latex, known as "cup washings," derived from the residua of latex thus washed out is kept separate during collection and delivery, and is coagulated separately. If, however, as is usual, it is desired to employ diluted latex for the preparation of rubber at the coagulating station, the cup washings may be mixed with the latex proper. It is the custom on probably most estates not to use the cup washings for the dilution of latex, but to dilute the latter with water, and to coagulate the cup washings separately. This procedure does not, however, appear to be the best. The fear, commonly held, that the cup washings, since when coagulated alone they usually give discoloured crêpe, will prejudice the crêpe or sheet to be prepared from the latex proper is groundless, provided that the diluted latex is carefully strained. The practice of coagulating cup washings separately, instead of mixing them with the general bulk of latex, has the effect of producing a sub-grade, which need not, in fact, be made at all, of crêpe of discoloured appearance and poor vulcanizing qualities. It will, of course, be understood that if the cup washings are to be mixed with the latex proper, the amount of water used for washing should not be so great as to produce undue dilution of the latex.

As ordinarily delivered at the coagulation station, latex has been diluted with approximately an equal volume of water and contains, say, 15-20 per cent. of rubber. The proportions of anti-coagulants mentioned below refer to such ordinary, diluted latex.

#### ANTI-COAGULANTS

It should be mentioned that, in the practical conduct of estate operations, the effectiveness of any anti-coagulant is largely dependent upon its being properly mixed with the latex. It has been found that, owing to failure of the solution and

latex to mix properly, comparatively little is gained by merely placing a small quantity of an anti-coagulating solution in the cups before the latter are placed under the trees. It is necessary to take steps to ensure admixture of the latex and anti-coagulant. It is not in all cases necessary to add the anti-coagulant at as early a stage as that represented by putting it in the cups: it may suffice, if the tendency to premature coagulation is not very strong, to introduce it into the latex in the pails, or even, when the inset of natural coagulation manifests itself only after the latex has been delivered at the coagulating station while awaiting coagulation, to introduce it in the coagulating tanks.

Among common chemicals which exercise an anti-coagulating effect on latex may be mentioned formaldehyde, sodium sulphite, ammonia, sodium carbonate, borax, sodium acetate, sodium phosphate. Of these substances, only the first four have ever been used in practice. And, of the first four, it may be said that only the first two have ever been widely used in plantation practice. Of these two, sodium sulphite, which was introduced into use later than formaldehyde, is the anti-coagulant which is now generally chosen. It is more effective than formaldehyde, and, as will appear below, is, unlike the latter, innocent of harmful effect on the quality of the rubber. The amounts of these materials which suffice to retard coagulation enough to avoid premature natural coagulation are much smaller than the amounts required in order to preserve the latex in a liquid condition indefinitely. Suitable proportions have in practice been found to be as follows:—

*Formaldehyde*.—Ultée<sup>1</sup> lays down, as a suitable amount, 20 c.cs. of a 2.5 per cent. solution of formalin per litre of latex. The present writer's experience indicated a similar proportion as suitable; the proportion laid down for use when it was desired to introduce a small amount of anti-coagulant into the cups being 500 c.cs. per tapper of a solution of 1 part of formalin in 500 parts of water (in the case of heavily yielding, old trees, the proportion to be increased somewhat).

*Sodium sulphite*.—Ultée<sup>2</sup> lays down 6 c.cs. per litre, or, say, 30 c.cs. per tapper's yield of a 20 per cent. solution of the crystalline, or a 10 per cent. solution of the anhydrous salt. The present writer has advised a similar proportion, viz. 500 c.cs. of a 1 per cent. solution of the crystalline salt per tapper.

*Sodium carbonate*.—Ultée<sup>2</sup> advises 10 c.cs. of a 10 per cent.

<sup>1</sup> *Archief*, 1917, 1, 406.

<sup>2</sup> *Loc. cit.*

solution of the anhydrous salt per litre of latex, and de Vries<sup>1</sup> 2 g. of the crystalline salt in 20 per cent. solution per litre of latex. In some trials made under the present writer's direction, 0.4 g. in suitable dilution per litre of ordinary tapper's latex was the minimum effective quantity.

*Ammonia.*—Campbell<sup>2</sup> gives 0.0056 per cent. of ammonia in the form of a 2 per cent. solution.

*Influence of anti-coagulants on vulcanizing properties.*—Concerning the influence of the above-mentioned anti-coagulants on the quality of rubber prepared from latex containing them in proportions such as those stated, the following results have been reported: Ammonia was not found to have any marked influence.<sup>2</sup> The tests referring to ammonia are, however, very limited in number. The effect of sodium carbonate was only very slight in experiments made by de Vries.<sup>3</sup> Such effect as it had was favourable; the tensile strength being improved by 0.0–0.04 kg./mm.<sup>2</sup>, the time of cure by 3–10 minutes, the slope by 0–1 units, and the index of viscosity by 0.02–0.04. In vulcanization tests made by the present author, on smoked sheet prepared from latex containing sodium carbonate, no appreciable influence of the reagent on the tensile strength, the slope or the rate of cure could be observed. Hence, it appears that the addition of sodium carbonate to latex for anti-coagulating purposes is unobjectionable. Sodium carbonate is an inexpensive and effective anti-coagulant. Its initial cheapness is, however, counterbalanced by the necessity for employing, in order to neutralize the carbonate, acetic acid in greater quantity than usual for coagulation.

De Vries<sup>4</sup> has shown that the presence of small amounts of sodium sulphite in latex has a small, but distinct, effect in improving the quality of the rubber. A quantity of 1 g. of the crystalline salt per litre of 15 per cent. latex improved the tensile strength of crêpe by 0.0–0.03 kg./mm.<sup>2</sup>, the time of cure by 5–10 minutes, the slope by 1–1.5 units, and the index of viscosity by 0.02–0.04. In the case of smoked sheet, *i. e.* in the case of a form of rubber in the preparation of which a larger proportion of the reagent added to the latex would be retained by the coagulum, the improvement in quality might be twice or three times as large as in the case of crêpe.<sup>5</sup> Van Heurn

<sup>1</sup> *Archief*, 1918, 2, 100.

<sup>2</sup> *Dept. Agric. Ceylon Bull.*, No. 23, p. 3.

<sup>3</sup> *Archief*, 1918, 2, 85–7.

<sup>4</sup> *Ibid.*, pp. 77–80.

<sup>5</sup> For less extensive and decisive results less favourable to sodium sulphite, vide *Dept. Agric. Ceylon Bull.*, No. 23.

and Bertels<sup>1</sup> draw attention to the fact that many samples of sodium sulphite sold in the East are of a low degree of purity. They recommend that the quality of the material in each drum should be checked by analysis before the material is put into use.

All published results as to the influence of formaldehyde on the vulcanizing properties agree in finding it to be harmful to a greater or less extent. The effect of formaldehyde is found by de Vries<sup>2</sup> to be greater in the preparation of sheet than in the preparation of crêpe. This is as would be expected from the circumstance that the reagent is less completely removed from the coagulum in the preparation of sheet than it is in the preparation of crêpe. When employed for crêpe in the proportion represented by 0.5 c.cs. of formalin per litre of latex, its effect is only small. When employed in larger quantities or for sheet, its effect may be serious. In the small proportion of 0.25-1 c.cs. per litre of latex its influence on crêpe was to affect unfavourably the tensile strength of the vulcanizate by 0.0-0.02 kg./mm.<sup>2</sup>, the time of cure by 2-5 minutes, the slope by 0-0.5, and the index of viscosity by 0.02-0.05. In the larger proportion of 2-4 c.cs. per litre, the corresponding unfavourable effects were 0.0-0.08 kg./mm.<sup>2</sup>, 5-15 minutes, 0.5-1.5, 0.03-0.09. In the case of a sample of smoked sheet, 0.5 c.cs. of formalin per litre extended the time of cure from 70 to 100 minutes and changed the slope from 37.5 to 39. Experiments by the Imperial Institute on sheet prepared from latex containing 0.5 per cent. of formalin showed the formalin to produce a similar reduction in the rate of cure.

In order to decide whether an antiseptic action on the part of formalin (cf. chapter, "Maturation of Coagulum") was the cause of its unfavourable effect on quality, or whether the formalin *per se* had a harmful effect, de Vries made further experiments. He showed that formaldehyde *per se* exercises a harmful influence on quality. This was shown in part by treating with formaldehyde rubber which was dry, and, hence, in relation to which there could be no question of biological changes influencing quality further. The time of cure of a sample of dry crêpe was extended from 130 to 140 minutes by soaking for twenty-four hours in a 10 per cent. formalin solution. Similarly, by exposing another sample of dry crêpe to the action of formalin vapour for twenty-four hours, the time of

<sup>1</sup> *Archief*, 1919, 3, 7.

<sup>2</sup> *Ibid.*, pp. 80-5.

cure was extended from 120 to 140 minutes. The following table shows the results of introducing powdered tablets of paraformaldehyde into the mix on the mixing rolls.

TABLE XXXVII

Percentage of formalin . . .	0	0.02	0.3	1.0
P <sub>B</sub> . . . . .	1.44	1.44	1.45	1.31
Time of cure (mins.) . . .	80	85	95	140
Slope . . . . .	35.5	35.5	36	36

Eaton and Grantham<sup>1</sup> had previously shown that formaldehyde *per se* influences the vulcanizing properties of rubber. They found that samples of rapid-curing crêpe (matured rubber, curing in 1-1.5 hours) were reduced in rate of cure by 0.25-0.5 hours as a result of immersion for twenty-four hours in 10 per cent. formalin solution. They showed, further, that when formalin was added in large quantities to latex used for the preparation of matured rubber (rapid-curing), its indirect action, as an anti-septic, was also important. De Vries concludes that it has such an indirect action even when added, to latex used for the preparation of sheet, in the small proportions which have been mentioned as suitable for the prevention of premature natural coagulation.

## LUMP

An experiment was made to determine whether the extent to which natural changes in latex short of the onset of coagulation have occurred influences the quality of the product obtained by acetic acid coagulation. Rubber prepared from latex coagulated at once was compared with rubber prepared after the latex had stood in a diluted condition for seven hours, and with rubber prepared after the latex had stood in an undiluted condition for five hours. It was found that the samples, in the order mentioned, showed a very slight increase in rate of cure as a result of the standing.<sup>2</sup>

When the latex arrives at the coagulating station, any pieces of lump floating in it are lifted out. Such pieces should then be broken up into small pieces and squeezed thoroughly, as, otherwise, latex contained in them is likely to be lost in the washing mills. The latex is sieved into large coagulating vessels.<sup>3</sup>

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 719-20.

<sup>2</sup> Whitby, *J. Soc. Chem. Ind.*, 1916, **35**, 493.

<sup>3</sup> In view of the importance of excluding all mechanical contamination from the product, it is desirable to use double ("two-deck") sieves; the lower mesh being closer (say, 64-mesh) than the upper one.



Any natural coagulum which it was not possible to lift out is thus removed. The lump is then converted into crêpe (*vide* section on Machining, Chapter VII). In order to secure the palest colour in the final product, it is desirable to convert the lump into crêpe at as early an hour as possible after its delivery at the coagulating station. If the coagulation station is situated at a long distance from the milling shed, it may not be feasible to crêpe the lump until the following morning. In such a case, the lump may be immersed overnight in a very dilute solution of sodium bisulphite. In order to secure a pale colour in lump crêpe, in addition to the steps just mentioned, soaking the freshly machined crêpe for several hours or overnight in a dilute (say, 0.5 per cent.) solution of sodium bisulphite can be recommended. The crêpe should not be rolled up, but should be laid loosely in the solution, so that the latter is able to get at all parts. The sodium bisulphite solution, if covered over carefully, will remain effective for, say, forty-eight hours.

On account of the circumstance that the price paid for crêpe rubber is at present largely determined by the degree of paleness of the product, the plantations find it advisable to aim at turning out the palest product possible. The line of procedure indicated above is adapted to achieve this aim. It is not, however, necessarily adapted to give rubber which comes out best in vulcanization tests. The present writer secured definite indications, in vulcanization tests, that lump left to stand overnight in the air before being crêped cured somewhat more rapidly than lump crêped on the afternoon of its delivery, although of a darker colour. This indication is in line with the results obtained in the study of the maturation of coagulum (*vide* Chapter VIII). De Vries<sup>1</sup> found rubber prepared from lump which had been left for one or more weeks before being crêped to cure more rapidly than usual, although not so rapidly as slab.

*Vulcanizing properties of lump rubber.*—Concerning the general standard of quality shown by lump crêpe as ordinarily prepared by the plantations: it appears to be similar to that shown by latex crêpe.<sup>2</sup>

<sup>1</sup> *Archief*, 1918, 2, 231.

<sup>2</sup> *Partial coagulation of latex.*—De Vries (*Archief*, 1917, 1, 178) found that the rubber obtained by coagulating latex only very partially differed quite noticeably from rubber obtained by coagulating it completely. In view of this, it might possibly have been anticipated that lump would differ similarly from latex crêpe. De Vries and Hellendoorn (*ibid.*, 223)

In the following table are shown the extreme and the mean results found by de Vries and Hellendoorn<sup>1</sup> on subjecting twenty different samples of lump crêpe, of lighter or darker shades of brown, to vulcanization tests. For comparison the correspond-

point out, however, that probably in most cases the greater portion of the lump grade is derived from coagulations more complete than the partial coagulation to which the above-mentioned experiments referred; a considerable portion of it is derived from the complete or nearly complete coagulation of the latex in occasional cups, and only a portion of it—in de Vries and Hellendoorn's opinion, only a small portion—by partial coagulation in the pails. Only in occasional cases did de Vries and Hellendoorn find lump crêpe to exhibit on vulcanization the characteristics of partial coagulum, *i. e.* low tensile strength and high rate of cure.

The results of the above-mentioned experiments of de Vries on partial coagulation may be given briefly. It was found that, when only so much acetic acid (*viz.* 1 part to 450–600 parts of rubber) was added to undiluted latex or only slightly diluted latex as to produce a clot containing only 15, or at the most 25 per cent. of the total rubber present, the rubber prepared from the clot differed markedly in its properties from either the rubber obtained from the uncoagulated residuum of latex or from the original latex by use of sufficient acetic acid to produce complete coagulation. The clot included the greater part of the oxidase of the latex: the rubber was yellow to brown in colour when dry, whereas the rubber from the remaining latex was white. (The present writer can confirm the fact that the oxidase is preferentially adsorbed by a partial clot.) The rubber obtained by partial coagulation showed a tensile strength lower and a rate of cure higher than the rubber from the remaining latex. It also showed a higher viscosity and a somewhat higher slope than the residual rubber. As regards its chemical composition, it showed high figures for all the non-caoutchouc substances usually associated with caoutchouc in the coagulum. The vulcanization coefficient at the optimum or standard time of cure was higher than at the cure giving a coincident stress-strain curve in the case of the residual rubber. The following table will illustrate these points. Each result is the mean of the results for five samples.

TABLE XXXVIII

	First clot.	Remainder.
Time of cure (mins.) . . . . .	90	115
P <sub>B</sub> . . . . .	1.35	1.51
Slope . . . . .	36	36.5
Index of viscosity . . . . .	2.16	1.78
Nitrogen (per cent.) . . . . .	0.64	0.47
Acetone extract (per cent.) . . . . .	5.6	2.7
Ash . . . . .	0.48	0.35
Vulcanization coefficient at standard cure (per cent.)	5.64	4.64

As to the full significance of these results, which show that non-caoutchouc constituents of latex are preferentially included in a partial clot, no investigations have hitherto been made.

<sup>1</sup> *Archief*, 1917, 1, 213.

ing figures for a collection of some 400 samples of latex crêpe are shown.

TABLE XXXIX

	Lump crêpes.		Latex crêpes.	
	Extremes.	Mean.	Extremes.	Mean.
Time of cure (mins.) .	90-125	110	75-150	115
P <sub>B</sub> . . . . .	1'24-1'50	1'35	1'24-1'50	1'38
Slope . . . . .	34'5-39	37	34-39'5	36'6
Index of viscosity .	1'36-1'94	1'705	1'36-2'08	1'668

Eaton,<sup>1</sup> in the examination of a smaller number (nine) of ordinary lump crêpes, also found lump crêpe to give results similar to those given by latex crêpe.

*Uniformity of lump rubber.*—These collections are not sufficiently large to enable it to be said whether the lump grade is more variable than the latex crêpe grade. There is, however, no doubt that, as in the case of the latex grade, it is possible for the plantations, by the adoption of suitable measures, considerably to reduce the variation in their product below that ordinarily found. It is customary to divide plantations for working purposes into sections, known as "fields" or "divisions," the rubber from each of which is collected and treated separately. Now, while for the successful management of the plantation and the control of field work it is usually desirable to have separate sectional records of the total yield, and of the percentages of the different grades in the total, it may be, and unless the sections are very large usually is, very undesirable to work up the latex and the lower grades from each section separately. In the interests of uniformity in the product, it is desirable to unite or blend the rubber from different sections. As to how the union may be effected in the case of latex rubber without sacrifice of the sectional records, will be indicated in the later section on Bulking Latex.

In the case of the lump grade, the union of rubber from different tapping sections is probably more important than any other single measure in combating variation. The author recommends that as far as possible the lump from all the sections of an estate should be worked up together. In order to secure sectional records, the lump from each section can be

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, pp. 352-3.

weighed before admixture of the lump from the different sections takes place. Owing to the irregularity in water-content of the lump as first received at the factory, it is not advisable to take the weight of the lump in its first stage, but after it has been converted into "sausages" in the "Universal" washer or into rough, thick crêpe on the masticating rolls. Experience will show what average allowance for water must be made in calculating dry weights from the weights taken. The day's crop of lump from the different sections is most satisfactorily blended in a "Universal" washing machine or other machine of the same type.

#### DETERMINATION OF THE RUBBER-CONTENT OF LATEX

In order to conduct the coagulation of latex satisfactorily, and to secure the most uniform product possible, it is necessary, as results quoted later will emphasize, to determine the rubber-content of the latex in the vessels at the coagulating station with a moderate degree of exactness. The methods which have been suggested for the determination of the rubber-content of latex are as follows: (a) The direct method, involving the rapid coagulation of a measured sample of the latex, the rolling or crêping of the coagulum, and the weighing of the rubber either in its wet condition or after rapid drying *in vacuo*. This method is commonly spoken of as "trial coagulation. (b) A nephelometric method. (c) A hydrometric method.

*Use of laticometers.*—The last of the methods mentioned has been the subject of a good deal of experimental work. It will be discussed first. In view of the fact that the specific gravity of rubber is lower than that of water, and of the observation that, at all events when speaking broadly, the higher the rubber-content of a sample of latex, the lower appeared to be its specific gravity, the employment of hydrometers (laticometers) naturally suggested itself as offering an attractively rapid and simple means for the determination of the rubber-content of samples of latex. A number of laticometers have been brought forward<sup>1</sup> and have been taken up rather widely by estates. The consensus of the results of published trials with such instruments is, however, to indicate that the instruments do not in practice give trustworthy

<sup>1</sup> Cockerill's hydrometer (Eng. Pat., 100,591 of 1916); a "latexometer" by Eaton (*Dept. Agric. F.M.S. Bull.*, No. 17, 1912, p. 47; *Agric. Bull. F.M.S.*, 1914, 2, 224, 317); a "Metrolac" introduced by the Rubber Growers' Association.

results. And de Vries, as the result of investigations into the specific gravity of samples of latex and of corresponding samples of serum, has concluded that the proposal to determine the rubber-content of samples of latex as ordinarily encountered in plantation coagulating stations by means of a laticometer is not only surrounded with practical difficulties, but is theoretically unsound.

The present author found in trials with hydrometers specially constructed for use in latex that trustworthy results could not be secured with such instruments. One of the chief practical difficulties in the application of the hydrometric method to the determination of the rubber-content of latex is the smallness of the range over which the specific gravity alters with change in the rubber-content. The specific gravity of latex with the highest rubber-content ever encountered is not less than 0.97. And in practice the extreme lower point of the range over which the instrument is required to read is higher than this, because (in the experience of Eaton<sup>1</sup> and of the author) latex with such a high rubber-content as that corresponding to the specific gravity just mentioned is so viscous that the instrument will not float in it. In order to get a reading, it is necessary to dilute such latex.<sup>2</sup> Because of the shortness of the range over which the specific gravity varies with change in the rubber-content, variations in the temperature from the temperature (say, 85° F.) at which the instrument is calibrated have a marked influence on the readings. De Vries<sup>3</sup> found that the influence of temperature on the result was greater, the higher the rubber-content of the latex. In a latex of specific gravity 0.9850 a temperature variation of 1° C. altered the reading by 0.00045, equivalent to 0.75 per cent. of rubber. In a latex of specific gravity 0.9950 the corresponding figures were 0.00031, 0.52 per cent. Further: because of the necessary sensitiveness of the instrument, a little material adhering to the bulb or stem throws the reading out seriously. The author found that if

<sup>1</sup> *Agric. Bull. F.M.S.*, 1916, 4, 153.

<sup>2</sup> It may be mentioned that experience of Eaton and of the author here referred to was with samples of latex in Selangor, F.M.S. It appears possible that the fluidity of latex differs in different districts. It appeared to the author that the latex in, at all events parts of, Ceylon possessed a much greater degree of fluidity than typical latex in Selangor. A hydrometer moved freely even in 40 per cent. latex in Ceylon. It is possible, too, that typical samples in the more northern parts of the Malay Peninsula have a greater fluidity or remains fluid for a longer period than latex in Selangor.

<sup>3</sup> *Archief*, 1917, 1, 246.

the instrument were allowed to bob up and down in the latex before coming to rest, the adherence of a small amount of latex to the projecting part of the stem might influence the result. But a more frequent source of error in this connection is the adhesion to the bulb or stem of particles of natural coagulum which may be present in the latex or on its surface.

Ultée,<sup>1</sup> Gorter<sup>2</sup> and Kerbosch<sup>3</sup> reported unfavourably on the results obtained by the use of hydrometers for the determination of the rubber-content of latex. Hartjens<sup>4</sup> made extended tests with laticometers ("Latexometers" and "Metrolacs"), and found the majority of readings to be 30-50 per cent. in error, and some readings to be even less accurate. In tests made by de Vries<sup>5</sup> the rubber-content as read by the laticometer ranged from 6-120 per cent. of the actual rubber-content in the case of a group of experimental trees, and from 70-106.7 per cent. in the case of observations made on twelve estates. Rutgers and Maas<sup>6</sup> agree as to the inaccuracy of readings of rubber-content given by laticometers. Their results are, however, somewhat more favourable to the instruments than the results already mentioned, as they find the error to be approximately constant in samples of latex of similar rubber-content.

*Specific gravity and rubber-content of latex.*—In addition to the practical difficulties which the determination of latex by means of reading its specific gravity by a hydrometer offers, an investigation of the specific gravity of the serum of samples of latex of different rubber-contents made by de Vries<sup>7</sup> has revealed a more fundamental objection to the use of laticometers. De Vries finds, in confirmation of the conclusion which earlier work<sup>8</sup> had indicated, that *in the case of undiluted latex* there is a linear relation between rubber-content and specific gravity, and, hence, that it is, theoretically, possible to determine the rubber-content of samples of undiluted latex by means of a suitable hydrometer. He finds, however, that, as had earlier been argued by Vernet,<sup>9</sup> such a relation does not exist in the case of diluted samples of latex such as are ordinarily dealt with in the plantation coagulat-

<sup>1</sup> *Cultuurgids*, 1911, 1, 209.

<sup>2</sup> *Jaarboek Dept. van Landbouw, Nijverheid en Handel in Ned. Indie*, 1911, p. 59.

<sup>3</sup> *Meded. over Rubber*, No. III, 1914, pp. 2-11.

<sup>4</sup> *Archief*, 1918, 2, 256.

<sup>5</sup> *Ibid.*, 1919, 3, 207.

<sup>6</sup> *Ibid.*, 1917, 1, 289.

<sup>7</sup> *Ibid.*, 1919, 3, 183.

<sup>8</sup> De Vries, *Archief*, 1918, 2, 241, 437. The conclusions of de Vries, *ibid.*, 1917, 1, 242, require modification.

<sup>9</sup> *Le Caoutchouc*, 1910, 4558.

ing stations, and, hence, that it is, theoretically, impossible, by means of a single hydrometer, to determine the rubber-content of the ordinary samples of latex on a plantation. De Vries found that, though the rubber-content and, correspondingly, the specific gravity of latex may vary over a rather wide range for samples from different groups of trees, the specific gravity of the serum remained nearly constant in the different samples. In observations (on, in different groups, from four to nineteen occasions) made on the latex from eight different groups of trees under different tapping conditions, it was found that, while the rubber-content of the latex ranged from 44.6-18.6 g. per 100 c.cs., and the specific gravity from 0.9674-0.9983, the specific gravity of the serum ranged only from 1.0226-1.0166.

Whereas the connection between the specific gravity and the rubber-content of undiluted latices is linear, and is represented by that portion of the line connecting a specific gravity of 1.02 (sp. gr. of serum, *i. e.* rubber-content = 0) and a specific gravity of 0.915 (calculated sp. gr. for rubber globules, *i. e.* rubber-content = 91.5 g. per 100 c.cs.) the extremes of which correspond to rubber-contents of, say, 20 and 45 (the limits actually encountered), the connection between the specific gravity and rubber-content of diluted latices, derived from undiluted latices of different original rubber-contents, is bi-dimensional, and is represented by the triangle connecting the ends of the portion of the line just mentioned and the point on the diagram corresponding to the specific gravity of water.

It appears<sup>1</sup> that the data connecting rubber-content and specific gravity of latex on which the "Latexometer" was constructed referred to latices derived by dilution from original, undiluted latex.

It seems possible that, despite the theoretical and practical difficulties attaching to the use of hydrometers, such instruments may be found to give moderately satisfactory results under some circumstances, as, *e. g.*, where the latex from a large area is bulked, so that differences in original rubber-content are largely neutralized, and where the degree of fluidity of the latex is such as to allow of good readings being taken.

*Nephelometric method.*—The employment of a nephelometric method for determining the rubber-content of latex has been suggested.<sup>2</sup> In preliminary experiments encouraging results

<sup>1</sup> *Vide* Eaton, *Dept. Agric. F.M.S. Bull.*, No. 17, 1912, p. 49.

<sup>2</sup> Whitby, *Plantation Problems of the Next Decade*, Batavia Congress, 1914.

were obtained. The latex was diluted to a fixed, high degree, and the turbidity compared with a standard turbidity. More extensive trials are required before a judgment can be passed on the feasibility of a nephelometric method of latex evaluation. A simple candle turbidimeter<sup>1</sup> might prove to be satisfactory for practical work.

Van Iterson<sup>2</sup> proposes to ascertain the rubber-content of latex by means of a little instrument in which the thickness of the film formed by placing a drop of latex, without dilution, between an ebony disc (below) and a glass disc (above), is adjusted, by altering the distance apart of the discs, until its appearance corresponds with the appearance of a standard represented by a ring of grey-white paint surrounding the discs. According to van Iterson, the instrument gave satisfactory results when tested with preserved latex. Hartjens,<sup>3</sup> in the course of extensive trials with fresh latex, finds the results given by the instrument to be quite unreliable, although he explicitly refrains from condemning the principle upon which the instrument is constructed.

*Trial coagulation.*—There remains the method of trial coagulation. In applying this method, the latex is thoroughly mixed, a measured sample (or samples) is withdrawn and is rapidly coagulated. For the purpose of withdrawing samples a dipper which when full to the brim holds the desired volume is most convenient.<sup>4</sup> A convenient volume is 250 c.cs. or 10 oz. In the case of very large tanks of latex, it is advisable to dip out samples from several points. The proportion of acetic acid suited to produce rapid coagulation of the samples is, say, 6 c.cs. of 1:1 acid per 100 c.cs. of 13.3 per cent. latex. When the samples are coagulated, the clots are converted into thin crêpe.<sup>5</sup> Since the amount of water present in the crêped samples will vary to some extent, it is necessary, in order to get exact and

<sup>1</sup> Vide Bulletin No. 151 of the United States Geological Survey. Cf. Woodman, Gookin and Heath, "The Nephelometric Determination of Small Quantities of Essential Oils," *J. Ind. Eng. Chem.*, 1916, 8, 128.

<sup>2</sup> *Meded. Delft*, 1916, p. 143; *Delft Communics.*, p. 17.

<sup>3</sup> *Archief*, 1919, 3, 77.

<sup>4</sup> Dippers can be made satisfactorily by a native fabricator of weights and measures, if the latter is supplied with a rectangular piece of paper representing the size of the sheet of metal corresponding to a cylinder of the desired volume, and is supplied, in addition, with a measuring cylinder for the purpose of making final adjustments.

<sup>5</sup> At coagulating stations where no crêping machinery is available, the clots are rolled out as heavily as possible. Such rolling is by no means as satisfactory as crêping, since the proportion of water left in the rubber varies more.



rapid results for the rubber-content of the latices from which the samples were taken, to dry the samples in a vacuum oven at an elevated temperature. Approximate results may, however, be obtained by weighing<sup>1</sup> the wet samples and making allowance for their presumed water-content. Such results are generally accepted as sufficiently accurate for ordinary purposes of factory coagulation.<sup>2</sup>

In order to avoid the onset of natural coagulation in the latex after its delivery at the coagulating station, it is necessary to determine the rubber-content as quickly as possible, so as to be able to proceed with coagulation with the least possible delay. When the latex from a large area is to be bulked in a tank, the delivery of the whole volume of latex in question may in some circumstances extend over a comparatively long period of time; and in such cases it would be advantageous if the determination of the rubber-content of the bulked latex could be taken in hand some time before the whole of the latex had arrived. Hartjens<sup>3</sup> has made some useful trials with the object of ascertaining whether the rubber-content of the bulked latex could be satisfactorily estimated by sampling the latex which was in the tank about half-an-hour before the delivery of latex was complete. Experiments on five estates where the latex of, in different cases, from 100-300 tappers was bulked, showed that the rubber-content as determined after one-third or after two-thirds of the tappers had delivered their latex did not differ seriously from that determined after all the latex had been delivered. (For data, see original.)

Kerbosch<sup>4</sup> proposes to estimate the rubber-content of latex by determining the total solids by drying 5 c.cs. of the latex at 105° and subtracting from the weight of the dry residue 9 per

<sup>1</sup> For taking weights use may be made of specially made sets of weights stamped with the proportion of water which it is necessary to add to the latex to which the sample refers in order to bring the latex to the standard rubber-content. The locally obtainable Chinese balances, such as are used by Chinese silversmiths, can be employed with satisfaction for taking sample weights. The balances are divided so as to read in hundredths of a tahlil (1 tahlil = 1.33 oz.), and are surprisingly accurate. The dipper used in conjunction with them is conveniently made to hold a multiple of 1 tahlil (cf. Farquharson, *Agric. Bull. F.M.S.*, 1916, 151).

<sup>2</sup> In view of the importance of securing uniformity of rubber-content and of coagulating conditions in general, it would seem desirable that plantations should move in the direction of greater exactness in the determination of the rubber-content of latex, and that consideration should be given to the advisability of introducing small vacuum ovens into all factories.

<sup>3</sup> *Archief*, 1917 1, 367.

<sup>4</sup> *Loc. cit.*

cent.—the quantity which his results indicated as a suitable allowance for the difference in weight between the total solids and the sheet from a given volume of latex.

Borrowman<sup>1</sup> measured in the case of a single sample of latex the relation between the rubber-content and the viscosity at different dilutions, and suggests that viscosity measurements might afford a practical means of ascertaining rubber-contents. The suggestion has not been tested, but would appear to be worth experimental examination.

#### DILUTION TO A STANDARD RUBBER-CONTENT

The rubber-content of the latex in the coagulating station having been ascertained, the next step in the preparation of satisfactory crêpe or sheet is to bring the rubber-content to a standard figure by dilution. A suitable standard dilution is 15 or 13.33 per cent.

*Relation of dilution to vulcanizing properties.*—Dilution to a standard rubber-content is necessary both in order to enable the coagulation to be made with certainty and exactness, and in order to avoid what has been shown to be a cause of non-uniformity in the vulcanizing properties of the product. That the degree of dilution of the latex influences the vulcanizing properties of the rubber has been shown by several workers. De Vries<sup>2</sup> concluded that dilution was without influence on the maximal tensile strength developed by the rubber on vulcanization (except possibly at extreme dilutions) and without influence of the slope of the stress-strain curve, but that it affected the rate of cure to a noticeable extent. The results obtained in two experiments repeated on a number of different days are summarized in the following table:—

TABLE XL

Experiment I.	Dilution (percentage rubber-content of the latex)	31-38	26	21	16	11
	Mean time of cure (mins.)	120	125	130	ca. 135	145
Experiment II.	Dilution (percentage rubber-content of the latex)	17	14	12	9	6
	Mean time of cure (mins.)	135	140	> 140	145	150

Eaton<sup>3</sup> finds dilution to produce a similar reduction in the rate of cure of crêpe. An investigation into the influence of

<sup>1</sup> *Rubber Industry*, 1911, p. 243.

<sup>2</sup> *Archief*, 1917, 1, 25.

<sup>3</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 192 *et seq.*

dilution on the vulcanizing properties and on the chemical composition of the rubber has also been made in Ceylon and at the Imperial Institute.<sup>1</sup> The general indication of the results is that dilution, even to the extent of 800 per cent., is without marked effect. But the results are somewhat irregular and inconclusive.

*Lime in the dilution water.*—It is occasionally found that the act of adding water for the purpose of bringing the rubber-content to the standard appears to bring about the setting-in of curdling, which makes it impossible to handle the latex successfully, although in general dilution retards the occurrence of natural coagulation. The present author has encountered this abnormal phenomenon on occasion, and was inclined to regard the effect in question as, in a sense, a mechanical one; the latex in question being in a state of incipient coagulation, and the effect of the introduction of water being, as it were, to bring about precipitation. For it was observed that trouble in this respect could often be avoided by pouring the latex *into* water (stirring gently meanwhile), instead of, as is customary, pouring water into the latex. Hartjens<sup>2</sup> appears to have shown that, at least in some cases,<sup>3</sup> a high lime-content in the water is responsible for the trouble, and that the addition of sodium oxalate (a calcium precipitant) to the latex would overcome it, although sodium fluoride (another calcium precipitant) was not found to be effective. That the phenomenon in question is connected with an abnormally rapid progress of the latex to a state of natural curdling is shown by the fact that the addition of the latex of recognized anti-coagulants prevented its occurrence.

*Systems of tanks for bulking latex.*—In order that the coagulation of the latex may be conducted most satisfactorily, and that the rubber produced may be as uniform as possible, it is necessary to avoid coagulating the latex in small lots—and to bulk the latex in large vessels. Estate practice in this connection is not yet by any means fully developed. In the early days of plantation rubber production, when the quantities of latex with which the coagulating stations had to deal were comparatively small, locally procurable glazed earthenware vessels, known as Siam or Shanghai jars, with a capacity of from twenty to fifty gallons, were, not unnaturally, used for the

<sup>1</sup> *Dept. Agric. Ceylon Bull.*, No. 32, 1917, p. 8.

<sup>2</sup> *Archief*, 1918, 2, 163.

<sup>3</sup> The experiments were made on an estate on the Malang Southern Watershed, Java.

reception of latex. As the crops increased, the number of such vessels in use was simply added to, so that in a large factory one might find a day's latex split up into fifty to a hundred separate portions, each in a separate vessel, and each requiring to be coagulated separately. With recognition of the desirability of bulking the latex, Siam and Shanghai jars are being replaced on well-conducted estates by large, specially constructed tanks; and it may be anticipated that the employment of vessels of the former kind, where large crops are in question, will soon be universally recognized on the plantations as out of date.

A complete system of tanks for the reception and coagulation of latex may be considered as consisting of tanks of three kinds, namely: first, a series of small tanks (receiving tanks); second, a large bulking tank; third, a series of sheet coagulation tanks. The different kinds of tanks may conveniently be placed at successively lower levels.<sup>1</sup> The latex is delivered into the receiving tanks from a platform at the back; the platform being outside the factory proper, so that the tappers do not have to enter the factory. The receiving tanks, which may be constructed in a row, with dividing walls one brick thick, are intended to receive the latex from different tapping sections. By measuring the volume of latex in each tank and dipping out a sample for trial coagulation, yield records for the individual tapping sections are obtained.<sup>2</sup> Where it is not desired to keep such sectional records, receiving tanks are unnecessary—the latex can be delivered directly into the bulking tank.

The bulking tank is conveniently a long tank lying in front of, and below the receiving tanks. The latex from the latter is run into it, is mixed, sampled and diluted to standard rubber-content. If crêpe is to be made from the latex, coagulation can be performed in the bulking tank, although, where sheet coagulating tanks are available, the use of the latter for crêpe coagulation offers certain conveniences.

The sheet coagulating tanks (*vide* Chapter VII) are placed on the ground level. Each is conveniently of about 100 gallons capacity. For the transference of latex from the bulking tank to the sheet tanks, the use of a cylindrical vessel, mounted on

<sup>1</sup> Locally built tanks of brick, rendered with cement, and lined with glazed tiles, have been found sufficiently satisfactory. But large sheets of glass would doubtless be preferable to tiles as a lining.

<sup>2</sup> Knowledge of the volume and rubber-content of the latex received makes the taking of wet weights of the crêpe produced (now customary in most factories) an unnecessary labour.

pivots, on a wheeled carriage, similar to the vessels often used for conveying latex on the plantation, is suggested. The addition of the coagulating acid to the latex can be performed conveniently and efficiently in such a vessel before the latex is tipped into the sheet coagulating tank.

Tanks auxiliary to the above-described system are acid tanks. These are placed on brackets at some distance above the ground. Suitably diluted acid for (a) crêpe (b) sheet coagulation is stored in them and can be drawn off as wanted.

#### COAGULATION BY ACETIC ACID

Although a large number of other coagulating agents and coagulating processes have been brought forward, yet, with insignificant exceptions,<sup>1</sup> the addition of a little acetic acid to the latex is the method universally employed for bringing about coagulation of the latex. Acetic acid, the use of which had been suggested by Biffen,<sup>2</sup> was the first coagulant to be used for plantation latex, and its choice has proved to be a fortunate one, for no more satisfactory coagulant has hitherto been found.

The minimal amount of acetic acid necessary for the production of clean coagulation varies to some extent with the degree of dilution of the latex.<sup>3</sup> Experiments concerning the influence of dilution on the possibility of securing complete coagulation with acetic acid, and concerning the amount of acid required for complete coagulation, have been made by Eaton<sup>4</sup> and others; but,

<sup>1</sup> Native holders of small plots of rubber have shown a predilection for alum as a coagulant. Eaton (*Agric. Bull. F.M.S.*, 1918, 6, 315) states that the unsatisfactory effect of this coagulant on the product can be traced in a vulcanizing examination of samples of sheet (unsmoked) put on the market by small holdings. The total amount of rubber produced on native holdings is, it may be mentioned, relatively only very small. It has (August, 1919) been made illegal to use alum as a coagulant in the Federated Malay States.

<sup>2</sup> *Ann. Bot.*, 1898, 12, 166. Biffen suggested the use of acetic acid as a result of observations on the preparation of rubber from *Hevea* latex by subjecting successive thin layers to the action of smoke, as practised in Brazil. For the generation of the smoke a preferred fuel in Brazil is *Attalea excelsa* nuts. It appears to have been generally assumed that the separation of the rubber from the latex by this smoking process was essentially due to evaporation of water from the latex. Biffen, however, concluded that acetic acid played a chief part. On passing the smoke of burning *Attalea* nuts through a condenser, he found the chief substance present in the aqueous layer to be acetic acid. He then observed that acetic acid added to latex produced satisfactory coagulation.

<sup>3</sup> The original statements of Parkin (*Circulars*, Nos. 12, 13, 14, *Royal Botanic Gardens, Ceylon*, 1899; *Science Progress*, 1910, 4, 596) in the contrary sense require correction (cf. Parkin, *I.R.J.*, 1913, 45, 1193).

<sup>4</sup> *Dept. Agric. F.M.S. Bull.*, No. 17, 1912, p. 10 *et seq.*

somewhat curiously in view of its practical importance, the subject has not been investigated as extensively and with as great a degree of exactness<sup>1</sup> as could be wished. Within the limits of dilution ordinarily encountered at the coagulating station (say, from 20 to 10 per cent. rubber-content), the proportion of acid required in relation to the weight of rubber to be coagulated may, for practical purposes, be considered as constant. According to the present writer's experience, the minimal quantity of acetic acid necessary for the clean coagulation of such latex overnight is 0.5 per cent. of the weight of rubber.<sup>2</sup> In practice it is usually advisable, particularly in the preparation of sheet (cf. section on Bubbles in Sheet, Chapter VII), to employ more (10–25 per cent. more) than this quantity. Ultée<sup>3</sup> recommends 0.66 per cent. of acid. The acid is diluted suitably, as mentioned later in connection with the preparation of crêpe and of sheet, before being added to the latex.

*Influence of excess of acetic acid on vulcanizing properties.*—It has been found that increase in the amount of acetic acid added to latex beyond the minimal quantity necessary to produce coagulation has little or no effect on the vulcanizing qualities of the product. This is a result of considerable practical importance, as in estate practice excess of acid is not always avoided. This result recommends acetic acid as against other and often cheaper coagulants (particularly mineral acids), an excess of which is often found to be harmful to the quality of the rubber (cf. section on Other Means of Coagulation, p. 147).

<sup>1</sup> Investigators have been content to describe the degree of completeness of coagulation by such terms as "complete," "nearly complete," and so forth, and have not stated it in numerical terms.

<sup>2</sup> According to Morgan (*The Preparation of Plantation Rubber*, London, 1913, p. 67: "Recommendations for the treatment of latex and curing of rubber," The Rubber Growers' Association, 1913) 0.33 per cent. of acid is sufficient for the coagulation of latex containing 30 per cent. of rubber or such latex diluted with as much as three volumes of water. In the present writer's experience, this proportion is insufficient to give perfectly clean coagulation. For example: in an experiment, a sample of latex containing 30 per cent. of rubber, when treated overnight with the above-mentioned proportion of acid, yielded a small amount of milky serum, from which a coagulum weighing 0.25 per cent. of the weight of the original coagulum could be obtained by the addition of a large amount of acid. The same sample of latex, when diluted with twice its volume of water, and treated overnight with the proportion of acid in question, gave a very milky-looking serum containing 0.6 per cent. of the rubber originally present in the latex. When four volumes of water were used for dilution, the incompleteness of the coagulation was very serious, and the surface of the coagulum was not firm, but was composed of loose flocules. In this last case, an increase of the acid by 25 per cent. still left approximately 1 per cent. of the rubber uncoagulated.

<sup>3</sup> *Archief*, 1917, 1, 407.

Eaton<sup>1</sup> found that increase of the acetic acid to twice the minimal proportion was without influence on the rate of cure of the rubber, and that, when employed in an excess of 400 per cent., its effect was to retard the cure by not more than a quarter of an hour. No unfavourable effect of excess of acetic acid on the tensile properties was observed. De Vries<sup>2</sup> found the following results: (a) With proportions of acetic acid ranging from the minimum to an excess of 300 per cent. no differences in tensile strength were observed. (b) The "slope" of all samples prepared as crêpe was not affected by excess of acetic acid. In one experiment—the result of which calls for confirmation—with smoked sheet a slightly unfavourable effect on the slope was observed. (c) Using 100 per cent. excess of acetic acid, the rate of cure was in some cases reduced by five minutes, but in others was affected only to a negligible extent. Using 300 per cent. excess, the time of cure was more noticeably influenced, being extended, for example, from 135 to 145 minutes. Ceylon experiments<sup>3</sup> agree with the above investigations in finding 100 per cent. excess acetic acid to be without appreciable influence on the quality of the rubber.

Eaton<sup>4</sup> records the results of experiments on the effect on vulcanizing properties of the use of acetic acid in a proportion too small to produce complete coagulation. He states that the rubber produced in cases where coagulation was incomplete cures slightly more rapidly than rubber produced in cases where coagulation is complete. The increase in the rate of cure is, however, very small in the case of crêpe, although more appreciable in the case of slab rubber. In the numerical presentation of the vulcanization results, it is to be seen only in one out of five crêpes. In view of the fact that higher concentrations of acid are less favourable to the occurrence of bacterial activity in the coagulum than are lower ones, it would be expected (cf. Chapter VIII) that a reduction in the amount of acid added below the minimal amount necessary for clean coagulation<sup>5</sup> would tend to lead to an increased rapidity of cure.

<sup>1</sup> *Agric. Bull. F.M.S.*, 1916, 4, 165; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 203 *et seq.*

<sup>2</sup> *Archief*, 1917, 1, 40.

<sup>3</sup> *Dept. Agric. Ceylon Bull.*, No. 23, 1916.

<sup>4</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 207.

<sup>5</sup> It may be remarked that, in the author's view, the term "clean coagulation" implies, not only the separation of a clear serum from the latex, but also the non-occurrence overnight of recognizable putrefaction in the coagulum or serum. It will, in fact, be found that, if the serum is quite clear, no obvious signs of putrefaction occur overnight.

## CRÊPE AND SHEET

Practically all the rubber is prepared in one of two forms: crêpe and sheet. In the preparation of crêpe, the wet coagulum is broken up (masticated) and washed on mills over the rolls of which a stream of water is running, and is then rolled out thinner into crêpe ribbons. In the preparation of sheet, the coagulum, which must have been made of a suitable slab shape, is rolled out between smooth rolls moving, in opposite directions, at equal speeds. The effect of this rolling is to squeeze out the (readily putrescible) serum and give a sheet of wet rubber, which, under suitable drying conditions, will dry without the occurrence of putrefaction. The drying is usually done in an atmosphere of warm wood smoke. In the case of crêpe the (putrescible) soluble, serum substances are removed with considerable completeness by the mastication, washing and rolling. The wet crêpe is most usually allowed to dry in the air. Sheet does not undergo any mastication.

## OTHER MEANS OF COAGULATION

The following notes may be added with reference to the influence on the quality of the product of employing other means of coagulation in place of the addition of acetic acid.

*Other acid coagulants.*—In experiments by Eaton<sup>1</sup> made with "slab" rubber, organic acids examined gave similar results to the result given by acetic acid. The acids examined were formic, citric, tartaric and oxalic.<sup>2</sup> The same may be said of the following locally produced coagulants, which owe their coagulating power to the presence of organic acids, namely: coco-nut sap which has been allowed to undergo acetic acid fermentation, fermented pine-apple juice, rice or Chinese vinegar. Mineral acids appear to yield rubber distinctly inferior to that yielded by acetic acid. The inferiority is very marked when an excess of the coagulant is employed. This has been found to be the case with sulphuric, hydrochloric and hydrofluoric acids.<sup>3</sup>

The case of sulphuric acid has been made the subject of rather extensive tests by Eaton. In these tests it was found

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 222 *et seq.*

<sup>2</sup> It may be mentioned that the weak acid, carbonic acid, for which great claims were made (Pahl, *Rubber Industry*, 1911, p. 234) is incapable of coagulating latex.

<sup>3</sup> Eaton, *loc. cit.*; *Dept. Agric. Ceylon Bull.*, No. 23, 1916.



that, whether the rubber were prepared in the form of slab, of sheet or of crêpe, the use of sulphuric acid for coagulation led to a marked retardation in the rate of cure. The time of cure of sheet, which, when prepared by acetic acid, was 2.5 hours, became extended by the use of sulphuric acid to 3 or 3.5 hours; and in the case of crêpe the prolongation produced by sulphuric acid was, say, from 3.25 to 4 hours. Martin<sup>1</sup> found that the addition of  $\frac{1}{8}$  per cent. of sulphuric acid to a rubber mix<sup>2</sup> on the mixing rolls had a striking influence in retarding the rate of cure. Esch,<sup>3</sup> and also Martin, point out that the presence of zinc oxide in a mix (as in the mix used in the Admiralty test) offers a special case in regard to the influence of sulphuric acid on vulcanization, owing to the fact that reaction would occur between the zinc oxide and the acid.

*Alum.*—Eaton finds that the effect of alum, a coagulant favoured to some extent by native rubber producers (*vide* footnote, p. 144), is even more unfavourable to quality than is sulphuric acid. The retarding influence of alum on vulcanization has also been shown by de Vries,<sup>4</sup> by soaking dry crêpe in aqueous solutions of alum.

Two methods of bringing about coagulation which have been proposed for practical use, and which do not involve the addition of a coagulant, may be mentioned, viz. freezing and anaerobic natural coagulation.

*Freezing.*—If latex is maintained for six to eight hours in a frozen condition in the chamber of a refrigerating plant in which ice is ordinarily prepared, it is found, when thawed, to have undergone coagulation.<sup>5</sup> Eaton<sup>6</sup> finds rubber prepared in any one form (slab or sheet or crêpe) by this (patented) procedure to be very similar in vulcanizing properties to that prepared in the same form by coagulation with acetic acid.

*Anaerobic natural coagulation.*—Investigations into the vulcanizing properties of the rubber produced by the anaerobic natural coagulation of latex<sup>7</sup> (*vide* p. 52) have been made by Eaton<sup>8</sup> and by de Vries.<sup>9</sup> All the samples of crêpe prepared

<sup>1</sup> *Rubber Industry*, 1914, p. 205.

<sup>2</sup> Composition of the mix: Barytes 60, sulphur 1.75, rubber 38.25.

<sup>3</sup> *Rubber Industry*, 1914, p. 134.

<sup>4</sup> *Archief*, 1918, 2, 93.

<sup>5</sup> The significance of this in regard to the theory of coagulation is not at the moment clear.

<sup>6</sup> *Loc. cit.*, p. 264.

<sup>7</sup> A suitable form of tank, with a heavy water-sealed cover, for the operation has been patented by M. Maude and W. S. Crosse.

<sup>8</sup> *Loc. cit.*, p. 283.

<sup>9</sup> *Archief*, 1917, 1, 5.

from the coagulum produced by overnight anaerobic natural coagulation, which were examined by Eaton, showed a rate of cure noticeably greater than that usually observed in crêpe prepared from coagulum produced by acetic acid. It would appear from this result as though maturation (cf. Chapter VIII) went on to a certain extent overnight. In the case of acetic acid coagulum, maturation does not take place overnight, but it would appear to be not improbable that it takes place in the case of anaerobic natural coagulum; for, as is pointed out elsewhere (p. 174), bacterial activity takes place more readily in natural coagulum than in coagulum produced by acetic acid, since acetic acid has an antiseptic effect.<sup>1</sup> As compared with bacterial activity in the aerobic coagulum which ordinarily forms a part of the rubber crop (*i. e.* lump), overnight bacterial activity in anaerobic natural coagulum would be likely to produce a greater proportion of the natural accelerator of matured rubber, by virtue of the greater amount of serum associated with the coagulum, and a smaller proportion, by virtue of the absence of air.<sup>2</sup>

De Vries has studied the vulcanizing properties of rubber produced by anaerobic natural coagulation when the latter is assisted by the addition to the latex of a small proportion (2.5–3 g. per litre of latex) of sugar (cf. p. 53). He finds in a considerable number of experiments that crêpe prepared by this means is closely similar to crêpe prepared from the same lot of latex by acetic acid in the usual way. The tensile strength, slope and viscosity of the rubber prepared with the aid of sugar was in nearly every case identical with the corresponding values for crêpe prepared by acetic acid; and difference in the rate of cure between the sugar- and the acetic-acid-coagulated crêpe, although observed in most cases, were only small, and occurred in both directions.

It would appear from a comparison of Eaton's and de Vries' investigations that natural coagulation in the presence of added sugar gives results noticeably different from those which it gives in the absence of added sugar. It should be mentioned that in Eaton's investigation strictly comparable samples (*i. e.* samples prepared from the same lot of latex) of rubber coagulated with

<sup>1</sup> Cf. Whitby, *Agric. Bull. F.M.S.*, 1918, 6, 374.

<sup>2</sup> The natural accelerating substances produced by maturation are probably derived from the latex proteins. As mentioned earlier, the exclusion of air favours the bacterial decomposition of carbohydrate in preference to that of protein.

acetic acid were not examined alongside the samples produced by anaerobic natural coagulation. The results, however, are of such a character as to leave little room for doubt that the crêpe prepared from coagulum obtained by the overnight anaerobic natural coagulation of latex to which no addition has been made cures more rapidly than crêpe prepared by acetic acid. De Vries' results prove that crêpe prepared by overnight anaerobic natural coagulation in the presence of added sugar has practically the same rate of cure as crêpe prepared by acetic acid.<sup>1</sup> It may be supposed that the acid produced by the fermentation of the added sugar acts like acetic acid in retarding maturation.

Barrowcliff<sup>2</sup> has discussed Eaton's results from the point of view of the uniformity of the product given by anaerobic natural coagulation. Eaton describes the uniformity of crêpe samples prepared by this method as "fairly good." A closer study of this method would appear to be desirable.

<sup>1</sup> A few results given by Eaton (*loc. cit.*, p. 291) for sugar-coagulated crêpe would appear to point in the same direction.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1918, **37**, 95 T.

## CHAPTER VI

### CRÊPE

*Sodium bisulphite*.—In order to inhibit the action of the latex oxidase, and thus to obtain an undiscoloured product,<sup>1</sup> it is now customary to add sodium bisulphite in small proportion to the latex prior to the introduction of the coagulant. The undiscoloured crêpe is white in colour when wet and freshly prepared. When dry it is of a pale amber colour. Many substances besides sodium bisulphite are capable of inhibiting the action of the latex oxidase, but in the case of almost all of them a sufficient quantity is not retained by the coagulum during its conversion into crêpe to prevent oxidative discoloration occurring while the crêpe is drying. It would appear that in the case of sodium bisulphite a sufficient quantity of the antioxidant may be retained (presumably adsorbed) after crêping to inhibit oxidase activity during drying.

The minimal amount of sodium bisulphite which it is necessary to add to latex of standard dilution, in order to ensure the non-occurrence of discoloration in thin crêpe prepared from such latex, varies somewhat from one sample of latex to another. In the present writer's experience a maximal quantity, which

<sup>1</sup> There is no reason to suppose that the vulcanizing properties of the rubber would be influenced by allowing the oxidase to produce discoloration.

The planters were led to direct their efforts to achieving *paleness* in their crêpe rubber because the market valuation of crêpe was (and still is) largely determined by the appearance of the product. It was perhaps inevitable, in view of the state of knowledge at the time, that in the early days of plantation rubber valuation of the product should be based largely on its appearance; but there is no doubt that the circumstance that raw rubber valuation is dominated by considerations of appearance is now and has for some time past been exercising a retarding influence on the development of the rubber industry.

Eaton (*Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 213) remarks with considerable justness: "The use of sodium bisulphite as a method of preparation of a pale, attractive-looking raw rubber has . . . created an artificial market, in respect to buying and selling of raw rubber." The present writer had earlier (*Rep. Batavia*, 1914, p. 165) drawn attention, more particularly with reference to smoked sheet, to the artificiality and unsoundness of the system of basing valuations on appearance and other extrinsic characters. And similar remarks have been made by other scientific workers (e. g. Morgan, *The Preparation of Plantation Rubber*).

never fails to produce satisfactory results in any sample of latex, is 0.75 per cent.<sup>1</sup> of the weight of the rubber. The quantity refers to the case of coagulum left, as is usual, overnight in the serum. De Vries gives 0.5-1 g., and Ultée 0.625 g. per litre of 15 per cent. latex. A convenient concentration of solution<sup>2</sup> in which to add sodium bisulphite to latex is 5 per cent.<sup>3</sup>

*Relation of sodium bisulphite to vulcanizing properties.*—The effect which the addition to latex of sodium bisulphite, in proportions such as those commonly employed, has on the vulcanizing properties of the rubber prepared from such latex has been the subject of several investigations, all of which agree in finding it to be unharmful. The first investigation was that of Beadle, Stevens and Morgan.<sup>4</sup> These authors found that the addition of sodium bisulphite to latex was without marked influence on the vulcanizing properties of the rubber. They found that on the whole it had a slight improving effect. In the case of the sample of sheet, and the sample of crêpe for which they quote numerical results, it appears that the rubber prepared with bisulphite cured with a noticeably greater rapidity than the rubber prepared without that chemical. In the case of two further samples, quoted in a later paper by Beadle and Stevens,<sup>5</sup> the rubber prepared with, and that prepared without bisulphite show no appreciable difference. Eaton and Grantham<sup>6</sup> found sodium bisulphite to be without effect on the vulcanizing qualities of crêpe, or to reduce the rate of cure slightly. The Delft

<sup>1</sup> In individual factories it is often found safe to fix a lower figure for the proportion of sodium bisulphite to be used. In any case, for the sake of uniformity in the product, the quantity habitually employed at any one factory should be fixed. In cases where the coagulum has to be transported from a sectional coagulating station to a main factory before being crêped, a larger proportion of sodium bisulphite is usually called for than in cases where it is taken direct from the coagulating vessels to the mills. Sodium bisulphite has a somewhat retarding effect on the rate of drying, particularly if employed in excess.

<sup>2</sup> Concerning the storage of sodium bisulphite solutions, see van Heurn, *Archief*, 1918, 2, 127. Concerning the analysis of the chemical, see van Heurn, *ibid.*, 12. Careful storage of sodium bisulphite in plantation factories, so as to avoid deterioration of the chemical by oxidation, is important. Consignments of very poor quality have at times been received. The quality of consignments should be checked by analysis.

<sup>3</sup> Convenient proportions in English measure are: 1 lb. to 2.5 gallons; add 4 oz. per gallon of standard latex, *i. e.* 2.5 gallons to 100 gallons of standard latex. Convenient proportions in metric measure are: 1 kg. in 20 litres of water; add 2 litres per 100 litres of standard latex.

<sup>4</sup> *I.R.J.*, 1913, August 2.

<sup>5</sup> *Rubber Recueil*, 1914, p. 357.

<sup>6</sup> *Agric. Bull. F.M.S.*, 1915, 3, 224, 444; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, 210.

Institute<sup>1</sup> finds rubber prepared with sodium bisulphite to be equal in quality to rubber prepared without.

De Vries<sup>2</sup> concludes that two opposed effects may be distinguished in regard to the influence of sodium bisulphite on quality: the direct effect of the chemical on vulcanization, and its effect indirectly by virtue of its antiseptic properties. The direct effect of sodium bisulphite is to improve all the properties—tensile strength, slope, rate of cure, index of viscosity—upon which de Vries judges vulcanizing quality. The indirect effect is to reduce the rate of cure. When the coagulum is rolled shortly after coagulation, the direct effect only of the chemical is observed; and there is always a small, but distinct, improvement in vulcanizing properties as compared with control samples prepared without sodium bisulphite. When the coagulum is left overnight, the antiseptic effect of the chemical, causing inhibition or retardation of bacterial activity in the coagulum, may neutralize the direct effect on the rate of cure, with the result that the product may cure only at the same rate as, or slightly more slowly than, the control. The following results for a particular series of samples illustrate this point:—

TABLE XLI

		Coagulum rolled.	
		After 2 hours.	After 24 hours.
Time of cure	Control	130 mins.	115 mins.
	Sodium bisulphite (0.66 per cent.)	125 „	120 „

The conception of two opposed effects would explain the slight irregularities in the results obtained by previous workers on the influence of the addition to latex of sodium bisulphite on the quality of rubber. As already indicated, de Vries sometimes found rubber prepared from coagulum left overnight with sodium bisulphite to cure slightly more slowly than control samples; but in the majority of cases it appeared that the bisulphite rubber left overnight still retained, although to a diminished extent, the advantage in rate of cure which it held a few hours after coagulation. In any case, it was found, in agreement with previous workers, that the effect of sodium bisulphite was in any event small. The results of employing

<sup>1</sup> *Delft Communics.*, p. 34.

<sup>2</sup> *Archief*, 1918, 2, 67.

the chemical as found by de Vries are shown in the following table:—

TABLE XLII

	0.33-0.66 per cent.	1.33 per cent.
Increase in $P_B$ . . . . .	0.00-0.05	0.00-0.02 ?
Decrease in time of cure (mins.) . . . . .	5-10	10-15
Improvement in slope . . . . .	1.00-1.5	1.00-1.5
Increase in index of viscosity . . . . .	0.03-0.15	0.06-0.20

In view of the consideration that the addition of acetic acid to latex containing sodium bisulphite may be presumed to give rise in the latex to sodium acetate and sulphurous acid, de Vries<sup>1</sup> investigated the effect of adding these last two materials separately to latex. (The latter of the two is a coagulant, and was used without acetic acid.) He found that the former produced a noticeable improvement in the rate of cure, but had very little or no influence on the tensile strength and the slope; and that the latter produced a noticeable improvement in the slope and a small improvement in the tensile strength, but had no influence on the rate of cure. Hence, the influence of each of the two substances in question is, as it were, complementary; and it may be supposed that the favourable effect of sodium bisulphite on (all) the vulcanizing properties is due, as regards the rate of cure, to the sodium acetate formed from it, and, as regards slope and tensile strength, to the sulphurous acid formed from it.<sup>2</sup>

Van Heurn<sup>3</sup> found the incorporation of 1 per cent. of sodium bisulphite (added on the mixing rolls in the form of powder) with the mix rubber 92.5 : sulphur 7.5 to accelerate the cure. When vulcanized at 147° for 1.5 hours, the mix gave in different experiments vulcanization coefficients of 3.39 and 3.91 as against 3.11 and 3.16 for control mixes without bisulphite.<sup>4</sup>

*Mixing acid and latex. Skimmings.*—The acetic acid for the preparation of crêpe is conveniently used in a 3-4 per cent. solution, where coagulation is conducted in small vessels (jars), and in 1.5 per cent. solution, where coagulation is conducted in large tanks. In the case of large tanks, it is advisable to use acid of the dilution last mentioned, and to organize with some

<sup>1</sup> *Loc. cit.*

<sup>2</sup> A similar conclusion applies to the influence of sodium sulphite (p. 129).

<sup>3</sup> *Meded. Delft*, 1916, p. 109; *Delft Communics.*, p. 208.

<sup>4</sup> In this connection reference should be made to the fact that Williams (*Rubber Industry*, 1914, p. 291; *Proc. Third Internat. Cong. Tropical Agric.*, London, 1914, p. 134) found the introduction of sodium bisulphite in powdered form on the mixing rolls to have a serious retarding influence on the vulcanization. Williams does not, however, state the composition of the mix used or other sufficient particulars concerning his tests.

care the introduction of the acid and the mixing, in order to ensure uniform admixture of acid and latex, without risk of coagulation setting in before mixing, skimming, etc., are completed. After the acid has been mixed with the latex, it is usual and advisable to remove froth from the surface by skimming.

The coagulum derived from the skimmings is worked up on the following morning in the same way as the main mass of coagulum. The rubber derived from the skimmings is usually classified as a sub-grade of Grade No. 1 (latex crêpe). Skimmings are obtained at two points, viz. (1) as mentioned above, after admixture of acid with the latex (second skimmings), and (2) before the addition of acid (first skimmings). The first skimmings consists of the scum and froth which is always or almost always found on the surface of the latex in a receiving vessel, after the latex, which has just passed through the sieve, has collected in the vessel. The first skimmings usually contains a considerable proportion of natural coagulum, and, hence, the crêpe derived from it (after the addition of acetic acid) usually has a tendency to discolour. The strength of this tendency varies in different circumstances. On the whole it seems best to class the rubber from first skimmings with the lump grade,<sup>1</sup> and, as in the case of that grade, to soak the crêpe in sodium bisulphite solution if a pale colour is desired. It seems best not, as is often done, to mix first skimmings and second skimmings. The crêpe from the latter should be of a paler colour, indistinguishable from Grade No. 1 crêpe, and should be classed with the latter.

#### CRÊPING

The wet coagulum, usually after being left in the serum overnight, is converted into crêpe on mills of the same type as, but smaller than those used for washing wild rubber preliminary to the manufacture of rubber goods. The rolls are commonly 12 in. in diameter and 15 or 18 in. in length. They rotate in opposite directions. A current of water flows over them continuously. The wet rubber passes through a series of different mills; the surface of the rolls having a different character in the different mills of the series. On the first mill of the series, or "battery," the coagulum is converted into a thick, rough crêpe. On succeeding mills the latter is converted into thin

<sup>1</sup> Tests made by de Vries (*Archief*, 1917, 1, 223) indicate that "scum" rubber is very similar to lump in vulcanizing properties.



crêpe ribbons, with, finally, an almost smooth surface, straight edges and few or no holes. Suitable styles of cuts on the rolls, and a suitable proportion in a given factory between the different styles, are considerations of some importance in economizing time and power.<sup>1</sup>

Batteries of mills as follows form convenient units: (1) masticator; the rolls are cut deep ( $\frac{3}{16}$  in. or 4.75 mm.), the cuts running axially, spirally or (best) forming diamonds; (2) rolls cut with spiral cuts in opposite directions, forming diamonds: cuts  $\frac{1}{10}$  in. or 2.5 mm. deep, and  $\frac{1}{2}$  in. or 1.25 mm. apart; (3) as (2), but cuts only half the depth; (4) smooth.<sup>2</sup>

The character of the metal used for the manufacture of the rolls is of some importance. Hard (chilled metal) rolls do not work well (except possibly on masticating mills), as, unless the surface is deeply cut, they do not grip the rubber well, and may even heat it. Hence, rolls of comparatively soft metal are called for. Not all soft rolls, however, are suitable. It is sometimes found that the soft rolls supplied soil the rubber owing to the presence of free graphite in them. The question of the character of the metal most suitable for crêping rolls forms the subject of a paper by van Heurn.<sup>3</sup>

It is advisable and usual to make the crêpe half the width of the packing-cases generally used. The latter are usually 19 in. wide. The width of the crêpe is adjusted by placing suitably spaced guides on the diamond-cut mills. The thickness of crêpe is suitably defined by stating the weight of a given length of standard width. A suitable thickness is that corresponding to a weight of 14 lb. when wet or, say, 11.5 lb. when dry per 100 ft. of crêpe 9 in. wide. Crêpe of this thickness dries in less than a fortnight.<sup>4</sup>

<sup>1</sup> As an example of such importance, a case with which the writer was concerned may be instanced. In this case the daily working hours of a factory producing crêpe were reduced from twenty-two to fourteen, by a rearrangement of the mills.

<sup>2</sup> The course of milling which in the author's experience is most economical of time and gives the neatest product is as follows: (a) the coagulum, cut into suitable slabs, passes three to four times through mill (1); (b) the thick crêpe from mill (1) is passed three times through mill (2) in the following way, namely: once singly, once doubled and with the edges bent over against the guides so as to produce straight edges, once singly; (c) the crêpe from mill (2) is passed once or twice (single strand) through mill (3); (d) finally, the crêpe is passed twice through the smooth rolls.

<sup>3</sup> *Archief*, 1918, 2, 1.

<sup>4</sup> Crêpe weighing 11 lb. wet per 100 ft. was found to dry in two-thirds, and crêpe weighing 20 lb. wet per 100 ft. in one and three-quarters of the time required by crêpe weighing 14 lb. wet per 100 ft.

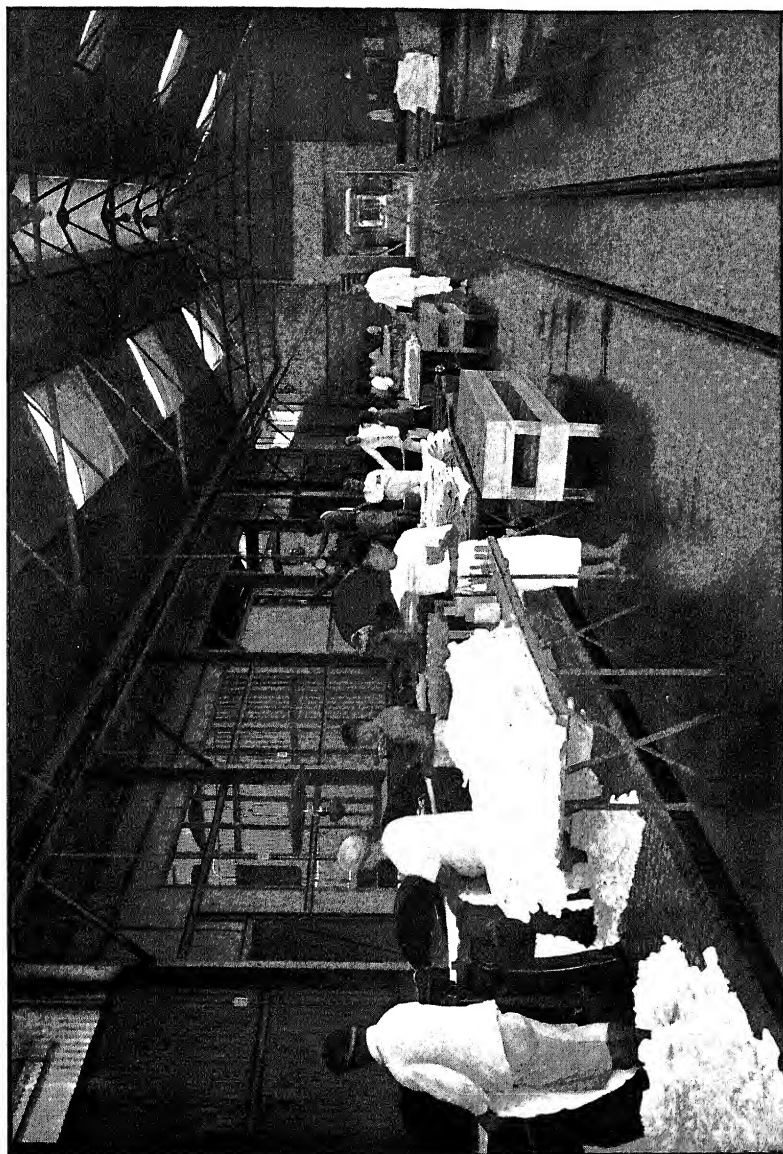


PLATE IV. Interior of Milling Shed (Wet Crépe in the foreground).

*Influence of working on vulcanizing properties.*—In view of the circumstance that the undue working of (dry) rubber on the (hot) mixing rolls in the course of the manufacture of rubber goods was generally accepted as being prejudicial to quality,<sup>1</sup> there was, when the preparation of crêpe from wet coagulum was undertaken on the plantations, a tendency to assume that mechanical treatment on the crêping mills must be prejudicial to vulcanizing quality, and should, so far as considerations of intrinsic quality were concerned, be restricted as severely as possible. It has now been established, however, that milling *per se*,<sup>2</sup> in the case of fresh, wet coagulum, is without serious influence on quality. Hence, there is no ground for fear that batches of plantation crêpe, which, on account of circumstances such as an unsuitable arrangement of the mills in a given factory, may be subjected to more than the minimal amount of working necessary to prepare crêpe from wet coagulum, will, within the limits possible in practice, suffer appreciably in quality.

That excessive working of the wet rubber has little or no influence on vulcanizing quality, was first shown by Eaton and Grantham,<sup>3</sup> and has since been confirmed by Campbell,<sup>4</sup> by de Vries,<sup>5</sup> and in further experiments by Eaton and Grantham.<sup>6</sup>

Eaton and Grantham's tests would appear to indicate that excessive rolling is entirely without influence on the quality of the rubber, but that very excessive mastication has a slight effect in reducing the rate of cure and possibly in reducing the tensile strength. Campbell found that, after the rubber had been through the rolls five to seven times, additional passages even up to the number of seventy had hardly any effect on the rate of cure and none on the tensile strength. De Vries also found that extra working to an extent much beyond any ever practised on estates was in most cases entirely without effect on the vulcanizing properties of the product, and in no case had more than a slight effect (5 mins.) on the time of cure. In his paper on the subject de Vries gives more detailed data as to the character of the rolls, the speeds of the different mills and

<sup>1</sup> For a discussion of the effect of excessive working on the mixing rolls, see Part II, p. 292.

<sup>2</sup> The influence of milling as resulting in the removal of serum solids is, of course, another question. Cf. *The Comparison of Crêpe and Sheet*, p. 184.

<sup>3</sup> *Agric. Bull. F.M.S.*, 1915, 3, 218.

<sup>4</sup> *Dept. Agric. Ceylon Bull.*, No. 24, 1916.

<sup>5</sup> *Archief*, 1917, 1, 17.

<sup>6</sup> *Dept. Agric. Bull. F.M.S.*, No. 27, 1918, 197.

the course of treatment through which the rubber was put, than do the papers by the other investigators mentioned.

*Influence of thickness of crêpe.*—Although differences in the extent of working to which different lots of wet rubber may be subjected in the preparation of crêpe have not *per se* any appreciable influence on quality, yet such differences may have an influence on quality if they connote (a) differences in the completeness with which the water-soluble serum solids are removed from the coagulum, (b) differences in the rate of drying, leading to differences in the extent to which maturation of the rubber (cf. Chapter VIII) occurs. This has been shown by Eaton,<sup>1</sup> who finds that rubber prepared by subjecting the wet coagulum to an amount of milling sufficient only to convert into thick crêpe cures more rapidly than rubber prepared from the same coagulum by conversion into thin crêpe. Thus, in one experiment, a sample of thick crêpe, which required twenty-two days to dry, had an optimum time of cure of 2.75 hours, while a corresponding sample of thin crêpe, which required only nine days to dry, had an optimum time of cure of 3.25 hours. No difference in the maximal tensile strength was noted between the samples.

As already indicated, two factors are concerned in determining the rate of cure of crêpe samples of different thicknesses, namely: the amount of serum solids left in the rubber, and the opportunity given for their decomposition, *i. e.* the length of the period of drying. From a given coagulum, let three portions of crêpe, as follows, be prepared: (a) thick crêpe made with the minimum of milling necessary; (b) thin crêpe; (c) thick crêpe prepared by rolling strands of (b) together. As regards the completeness with which the water-soluble serum solids have been washed from the coagulum: this is less in the case of (a) than in the cases of (b) and (c). As regards the period of drying: this is shortest in (b) and longest in (c).<sup>2</sup> Now, Eaton finds that

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 147, *et seq.*

<sup>2</sup> In an actual experiment, after eleven days' drying (a) contained 0.9, (b) 0.0, (c) 8.3 per cent. of water. Thick crêpe prepared by rolling strands of thin crêpe together is known on the plantations as "blanket" crêpe. Although, as just indicated, it dries more slowly than thick crêpe prepared directly (Sample a), initially it contains less water than direct thick crêpe. The effect of extra milling is to squeeze water out and at the same time to associate the remaining water more closely with the rubber—to squeeze it in, as it were. This may be gathered from experiments by Eaton (*loc. cit.*, pp. 150, 156, 202) and is in accord with experiments made by the present writer, who found, *e. g.*, that a portion of a sample of wet crêpe containing 15.8 per cent. of water, when subjected to ten extra passages through a mill, had its water-content reduced to 13.3 per cent., but took twice as long to dry.

in such a series the order in which the samples stand as regards rapidity of cure is (a), (c), (b); the differences in time of cure from one sample to the next being generally a quarter of an hour. Hence—it will be observed—the longer period of drying during which (c) remained wet had the effect of permitting maturation of the coagulum, with the result of hastening the rate of cure as compared with sample (b), which contained the same amount of serum substances but remained wet for a much shorter period; but that, despite the longer period during which (c) remained moist, it did not, on account of the more complete washing to which it had been subjected, develop as great a rate of cure as (a). Other investigations<sup>1</sup> confirm the conclusion that direct thick crêpe cures more rapidly than thin crêpe.

*Drying thick crêpe.*—Despite the noticeable superiority of direct thick crêpe over thin crêpe in regard to rate of cure, the preparation of such thick crêpe has not commended itself to the plantations. Thick crêpe of the type in question—*direct* thick crêpe—is prepared, as already indicated, by rolling the coagulum out to a smaller extent than in the preparation of thin crêpe and then allowing the product to dry naturally in the air. The period of time required for the drying of such thick crêpe is much more protracted than the period for the drying of thin crêpe. This extension of the drying period is found in practice to render it impossible to prepare a pale, uniform-looking product such as can be obtained when the crêpe is made thin.

Some results of the more extended drying period are as follows:—(a) the rubber has a more pronounced tendency to suffer discoloration. In order to overcome this tendency, the addition to the latex of an increased proportion of sodium bisulphite would be required; and this, again, would tend to prolong the drying period still further. (b) Either the drying sheds become congested, or it is necessary to build extra sheds. (c) Chromogenic fungi grow in the rubber and produce coloured spots on it. These difficulties can be avoided by drying the rubber more quickly by artificial means; but such a reduction of the drying period naturally sacrifices the advantages of the maturation which would occur during the longer period of drying, although it would retain the advantages which the thick crêpe possessed by virtue of the incompleteness of the removal of water-soluble serum solids from it. In point of

<sup>1</sup> Dept. Agric. Ceylon Bull., No. 23, 1916, p. 15.

fact the artificial drying of such thick crêpe has never been practised.<sup>1</sup>

The preparation of direct thick crêpe was abandoned, chiefly on account of trouble with spots, not very long after it was first taken up by the plantations. Such thick crêpe as is now prepared is seldom or never "genuine," i. e. direct, thick crêpe; it is usually prepared by converting the coagulum into thin crêpe, drying the latter in a vacuum or hot-air drier, and converting the dry, thin crêpe into thick crêpe. The product is identical in vulcanizing properties with thin crêpe (cf. section on Vacuum Drying).

#### COLOURED SPOTS

The cause of the appearance of coloured spots in crêpe has been studied particularly by Sharples,<sup>2</sup> who has shown that such spots are due chiefly to common saprophytic fungi, most of which belong to the genera *Penicillium* and *Aspergillus*. The commonest spots are blue-black ones and orange ones, but others also occur. It is probable that all wet rubber is infected with the spores of fungi, which are capable, if permitted, of germinating and grow vigorously, producing spots. If the rubber dries reasonably quickly, the spores do not develop sufficiently to produce spots.

It is now well understood on the plantations that the avoidance of coloured spots in crêpe is, in practice, a question of ensuring that the drying period shall not be unduly prolonged. As illustrative of the dependence of spot development on the rate of drying, the following experience may be mentioned: If a length of wet, freshly-prepared crêpe of medium thickness was left folded up for twenty-four hours before being hung up in the drying shed, it was not uncommonly observed to develop coloured spots all over except along the transverse strips corresponding

<sup>1</sup> If it were undertaken, it could best be done by a drying system employing unheated, dry air (such as the Normair system), or one employing moist, warm air (such as the Hunter Kiln), which, unlike vacuum driers (as ordinarily employed) or hot-air driers, would not have the effect of softening the rubber, and would allow at least some maturation to take place. Such systems might, indeed, allow a good deal of maturation to go on, as the temperature might well be adjusted approximately to that which is optimal for bacterial activity. Direct thick crêpe dried artificially by a system, which would not subject it to too high a temperature, and would dry it less quickly than vacuum—and hot-air—driers usually do, would appear to have a good deal to commend it.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 19, 1914; *Proc. Third Internat. Cong. Tropical Agric.*, London, 1914, p. 172.

to the ends of the folds; that is to say, the slightly more favourable drying conditions which the rubber at the ends of the folded-up crêpe had enjoyed during the first twenty-four hours had been sufficient to determine the non-appearance of spots.

Owing to the presence of fungal spores, it is usually possible to bring about a development of coloured spots in unspotted, dry crêpe, by moistening the rubber. Hence, it may occasionally happen that crêpe, which when packed was free from spots, develops coloured spots later, owing to the wood of the packing-cases being damp originally, or owing to the rubber getting damp during transport or in storage. In such a case which came to the attention of the writer, packing-cases of unspotted, pale crêpe had been left for six weeks standing on a cement floor in the tropics. The lengths at the bottom of the cases were found to have developed large, coloured spots. The highest percentage of moisture found in any of the lengths which had developed spots was 2.4. Some of the spotted lengths contained only 1 per cent. of moisture.<sup>1</sup>

*Influence of spots on vulcanizing properties.*—There is a little difficulty in subjecting to a simple, direct test the question as to whether the development of chromatic spots influences the quality of rubber, on account of the circumstance that, since the drying conditions suited to the production of spots are different from those suited to their avoidance, other factors than the spots themselves are likely to influence the samples under comparison. Eaton has, however, made some experiments, which approach the question indirectly, and the tendency of which is clearly to indicate that the development of spots may affect the rate of cure unfavourably. Sharples<sup>2</sup> had concluded that the fungi responsible for spotting subsist on the protein constituents of the rubber by virtue of a production of proteolytic enzymes. Now, it has been found that the presence of proteins in rubber is favourable to the vulcanization process, and that the products derived from the rubber proteins by anaerobic bacterial action are extraordinarily favourable to the vulcanization process (cf. Chapter VIII). Eaton's experiments make it appear that the growth of spot-producing fungi is destruc-

<sup>1</sup> Cf. Eaton, *Agric. Bull. F.M.S.*, 1917, 5, 177; *I.R.J.*, 1918, p. 184; cf. also photographs shown by van Heurn (*Archief*, 1918, 2, 119, 120) of crêpe samples which have become pigmented in strips coinciding in position with those parts of the rubber which were in contact with damp planks in packing-cases.

<sup>2</sup> *Loc. cit.*

tive in part of the nitrogenous substances which accelerate vulcanization.

Eaton concluded that the presence of air or oxygen was necessary for the development of spots. In one series of experiments he allowed wet, thin crêpe to undergo "maturation" (bacterial decomposition of rubber protein) under two different conditions, viz. (a) by pressing it into a block, (b) by merely rolling it into a cylinder, so that air could get at the surface of the crêpe. Under the first of these two conditions no pigmentation of the rubber occurred; under the second, marked pigmentation occurred in every experiment. Sample (a) showed in every case a greater rapidity of cure than a control, unmaturred crêpe. The reduction in the time of cure was 0.5-1 hour; the time of cure of the control being, on Eaton's method of testing, 3-3.25 hours. Sample (b) also, in seven out of ten experiments, cured more rapidly than the control, but not so rapidly as sample (a). In different experiments (b) was 0.25-1 hour slower than (a).

It was clear that the effect of spot development had been unfavourable to the maturation process. A further series of experiments, on the influence of pigmentation on rapid-curing crêpe ("slab" crêpe), in which maturation had already proceeded to its limit, appears to show that the spotting fungi are able to destroy in part or, less likely, partly to neutralize the effect of the already-formed accelerating substance derived from protein decomposition, and thus to diminish the rate of cure. Portions of matured crêpe, which had been hung up to dry, and in which no spotting had taken place, were compared with portions of the same samples, containing initially 25-27 per cent. of water, which had been rolled up and allowed to remain so for 1½-2 months, and in which a marked development of pigment had occurred. It was found that, while the former (control) portions gave their optimum cure in ten experiments in 1.25 hours, the effect of pigmentation in the latter portions had been to extend the time of cure to 2-2.25 hours. The development of pigment in the latter portions had brought about a loss of weight—presumably due to protein decomposition—of 1-5.4 per cent.

#### DRYING CRÊPE

Sometimes crêpe is dried by artificial means, but more generally it is hung in large sheds and allowed to dry naturally. In Malaya and Sumatra the latter method (air drying) is followed



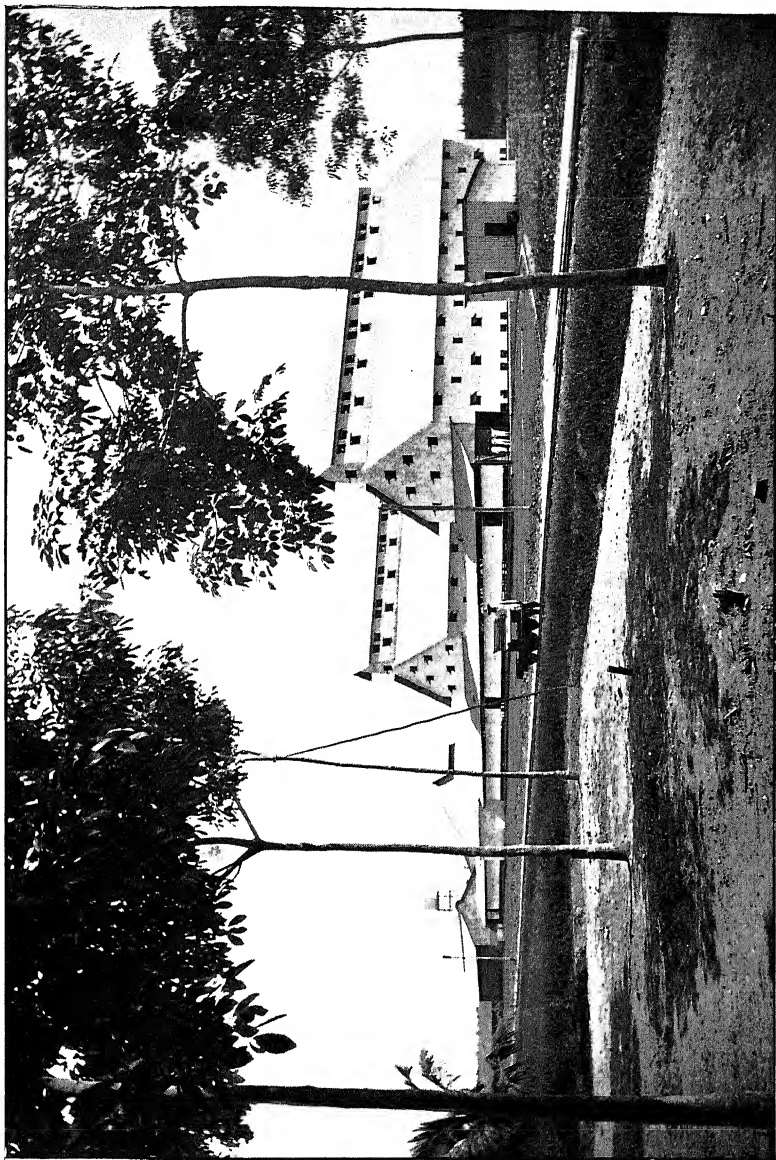


PLATE V. Crêpe Drying Sheds (on the right).

almost exclusively. In Ceylon artificial drying, by means of vacuum or hot-air driers, is frequently employed. Under normal circumstances, in a properly constructed and properly managed drying shed, thin crêpe of the customary thickness is dry, *i. e.* the rubber has become translucent and entirely free from white, opaque spots, within a fortnight.

Crêpe drying sheds (two are pictured on the right of Plate V) are best placed in a dry, open situation. The detailed advice, concerning their construction and management, given by van Heurn,<sup>1</sup> can be commended. The sheds should be constructed and operated so as to secure the best possible ventilation in them. They should be closed up tight at a comparatively early hour in the late afternoon, and should not be opened again until a comparatively late hour after sunrise, as the degree of humidity of the atmosphere of rubber-producing countries becomes high at an earlier hour in the evening, and remains high until a later hour in the morning than is, perhaps, generally supposed.

*Moisture-content of crêpe and the atmospheric humidity.*—The rate of drying of free-hanging crêpe rubber and its relation to the degree of atmospheric humidity have been studied by van Heurn<sup>2</sup> and Whitby.<sup>3</sup> The initial water-content of crêpe, after the surface moisture has drained away, is 10–15 per cent. It is found that the rate of drying is greater during the daytime than at night, and that, after the moisture-content has fallen to approximately 1 per cent., *i. e.* after three to five days, the crêpe shows a negative rate of drying during the night. The disappearance of the last 1 per cent. of water from the rubber occupies approximately as long a period as the time taken for the reduction of the water-content from its initial value to 1 per cent.

After the rubber has become dry and ready for shipment, as judged by the customary criterion, *i. e.* the absence of opaque spots, the moisture-content of free-hanging samples, and, to a smaller extent, of folded samples,<sup>4</sup> shows great fluctuations in response to fluctuations in the degree of atmospheric humidity. As illustrating the extent to which the moisture-content of free-hanging, "dry," thin crêpe may fluctuate, it may be mentioned that in a sample on which observations were made<sup>5</sup> the moisture-content was on one day 0.10 per cent. at 5.30 p.m. (atmospheric temperature, 30.8°; relative humidity, 58), and

<sup>1</sup> *Archief*, 1918, 2, 121–2.

<sup>2</sup> *Ibid.*, 1918, 2, 22, 115.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1918, 37, 278 T.

<sup>4</sup> Cf. de Vries, *Archief*, 1918, 2, 858.

<sup>5</sup> Whitby, *loc. cit.*

on the following day 0.51 per cent. at 8.45 a.m. (atmospheric temperature, 26.1°; relative humidity, 89.5). The moisture-content of free-hanging samples of crêpe (and of sheet) was found to exhibit a diurnal change, which showed a general parallelism with the degree of humidity of the atmosphere; it was, on a normal day in the Eastern tropics, markedly higher in the early morning than in the afternoon.

Krayenhoff van der Leur<sup>1</sup> has made some laboratory observations on the moisture-content of various samples of raw rubber when in equilibrium with air of different degrees of humidity and at different temperatures. Her results regarding the equilibrium water-content of raw rubber in the forms of crêpe and sheet are shown in the following table:—

TABLE XLIII

Humidity (per cent.)	Temperature 16°.					Temperature 30°.			
	100	89	77	49		100	89	77	49
Crêpe	2.80	0.89	0.39	—		4.54	1.06	0.37	—
Sheet	1.85	0.88	0.31	0.23		2.88	0.76	0.44	0.24

It follows from these results that the equilibrium water-content of raw rubber is lower in temperate climates than in the tropics.

*Artificial drying of crêpe.*—Where the vacuum drying of rubber is practised, it is usual to employ an elevated temperature, of 130–170° F., in addition to the vacuum of 27–28 in. The time required for the drying of thin crêpe under such conditions is about one hour. The softened, dry product is usually converted into thick crêpe. In the hot-air drying of crêpe, the wet rubber is exposed to a current of hot air, at 120–140° F., for, say, 5–8 hours.<sup>2</sup> The softened, dry rubber thus obtained is usually converted into thick crêpe. The thick crêpe produced in connection with vacuum or hot-air drying is sometimes known as “gristly” crêpe.

Eaton<sup>3</sup> and also Campbell<sup>4</sup> conclude that the artificial drying of crêpe by the methods just mentioned is without appreciable influence on the vulcanizing properties of the product.

<sup>1</sup> *Meded. Delft*, 1916, p. 473; *Delft Communics.*, p. 40.

<sup>2</sup> The systems generally employed are the “Colombo Commercial” and the “Walker,” Ceylon.

<sup>3</sup> *Agric. Bull. F.M.S.*, 1916, 4, 219; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, 160.

<sup>4</sup> *Dept. Agric. Ceylon Bull.*, No. 24, 1916.

Other drying systems have been suggested at various times, but have not been adopted to any noticeable extent.<sup>1</sup>

#### LOWER GRADE CRÊPE

As already stated, the so-called lower grades prepared on the plantations comprise as recognized representatives "lump," "scrap," "bark" and "earth" rubber. Lump has already been discussed.

In order to prepare from tree scrap, from bark shavings or from earth rubber, crêpe rubber free from the materials (bark and earth particularly) with which it is in the first place contaminated, more prolonged milling and washing than in the case of Grade No. 1 or of lump is, naturally, necessary. The removal of the bark, etc., is performed more satisfactorily on a special washing mill than on the ordinary masticating rolls.<sup>2</sup> The special mills most generally employed<sup>3</sup> consist essentially of two large rolls, provided with deep, corresponding corrugations, and working in a vessel into which water is sprayed. A charge (about 150 lb.) of shavings containing 10 per cent. of wet rubber requires about forty-five minutes' treatment to complete the washing away of the bark and the amalgamation of the rubber.

It is possible by the use of such washers to produce crêpe of very satisfactory cleanliness, even from bark shavings, which are more difficult to wash than the other low grades; so that

<sup>1</sup> In the "Normair" system, air, at ordinary temperatures, which has been rendered dry by passing over refrigerating coils, is employed. The "Hunter Drying Kiln," which appears to be found satisfactory in a number of rubber manufactories, and which, with the intention of preventing the formation of an almost-impervious outside layer at an early stage of the drying, employs *moist*, hot air, has not, so far as the author knows, been tried on the plantations. Such systems as those just mentioned are less rapid than the vacuum and hot-air systems, but, unlike the latter, they do not necessitate a re-crêping of the dry rubber.

<sup>2</sup> An example of the greater effectiveness of a special mill (the "Universal" washing machine) as compared with the ordinary masticating mills in cleansing the low grades is given by Ultée (*Archief*, 1919, 3, 412). Samples taken at monthly intervals over a period of eight months from an estate (A) employing a special mill, and from an estate (B) employing the ordinary mills showed the following mean figures for ash:—

Bark crêpe: A, 0.78; B, 0.82.

Earth crêpe: A, 1.46; B, 2.22 per cent.

The percentage of ash, it will be noticed, is, as would be expected, in any case higher in these grades than in latex crêpe.

<sup>3</sup> Namely, the Werner-Pfleiderer "Universal" washing machine. Locally-manufactured machines on similar lines have been introduced in recent years.

careful inspection with the naked eye will fail to detect any particles of bark or sand, although, possibly, some may be detected with a lens. Not all estates, however, succeed in achieving this degree of cleanliness in their low grades. After being washed on the special washer, the rubber is converted into crêpe by a similar course of milling to that followed in the case of latex rubber. It is customary, however, not to roll scrap, bark and earth crêpes out as thinly as latex crêpe.

*Vulcanizing properties of low-grade crêpes.*—The low-grade crêpes have not received as close attention as has latex crêpe. So far as can be judged from the limited surveys of low-grade crêpes which have been made, it would appear that the rubber of these grades tends to be somewhat more variable in vulcanizing properties than rubber of the latex grade. The wider range of variation observed is probably due to the fact that some estates do not pay sufficient attention to their low grades. As Eaton points out,<sup>1</sup> "there is no reason why lower grades of good quality—apart from colour—should not be obtained on most estates, with proper collection at short intervals, careful storage where necessary, and treatment in a good washing machine as soon as possible after collection."

The following summarizes the results obtained by de Vries and Hellendoorn<sup>2</sup> on subjecting thirty-one samples of scrap crêpe to vulcanization tests :—

TABLE XLIV

	Limits.	Mean.
P <sub>B</sub> . . . . .	1.09-1.46	1.31
Time of cure (mins.) . . . . .	70-135	107
Slope . . . . .	36-41	39
Index of viscosity . . . . .	1.32-1.85	1.61

If these figures are compared with those obtained by the same authors for a collection of about 400 samples of latex crêpe (Table XXXIX, p. 134), it may be gathered that the mean figures for scrap-crêpe samples do not differ very greatly from those for latex-crêpe samples. Two points, however, present themselves as worthy of note :—

(1) The first is that, although in general scrap crêpes show a similar tensile strength to latex crêpes, in occasional instances

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1018, p. 360.

<sup>2</sup> *Archief*, 1917, I, 217.

their tensile strength is markedly low. This is also found to be the case by Eaton.<sup>1</sup> It would appear that the bark grade and particularly the earth grade, as produced in the East, are distinguished from the latex grade by including a good many samples showing comparatively poor tensile properties, although they also include some samples showing good tensile properties. The tensile strength of five samples of bark crêpe examined by de Vries and Hellendoorn was between 0.97 and 1.12, and of three samples of earth crêpe between 1.13 and 1.21. The tensile strength of eight samples of bark crêpe examined by Eaton ranged from 0.78 to 1.48, and of five samples of earth crêpe from 0.88 to 1.27.

(2) A striking feature of the low grades which appears in de Vries and Hellendoorn's tests on these grades is their poor slope.<sup>2</sup> De Vries expresses the opinion that the slope offers the most useful basis on which to judge the quality of low-grade crêpes. Whereas for latex crêpe the slope ranged from 34-39.5 (mean, 37.45), for thirty-one samples of scrap crêpe it ranged from 36-41 (mean, 39), for five samples of bark crêpe from 42-47, and for fifteen samples of washings crêpe<sup>3</sup> from 37.5-53.5. (For four samples of earth crêpe the range was only from 37-38.)

It would appear that, considering the low-grade crêpes turned out by the plantation as a whole, while much of the rubber is similar in vulcanizing properties, although possibly more variable than latex crêpe, it comprises a considerable number of samples the vulcanizates from which are distinctly inferior to those from latex crêpe in those essential mechanical properties represented by the figures for the maximal tensile strength and slope.

On some estates two or more lower grades (say, scrap, bark and earth rubber) are mixed to form a product known as "compound" or "compo" crêpe.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> As explained in Part II, slope signifies the resistance which the vulcanized product offers to extension at high stresses. The higher the figure for slope, the poorer the quality of the rubber in this regard.

<sup>3</sup> Prepared from the very diluted latex obtained by washing out jars, pails and perhaps cups.

## CHAPTER VII

### SHEET

In the preparation of sheet, the wet coagulum is not, as in the preparation of crêpe, broken up on mills, but, having been formed in slabs of suitable dimensions, is merely rolled out, by being passed between rolls moving at even speeds in opposite directions. Although the rolling has the effect of removing most of the serum from the coagulum, it does not remove the serum as completely as it is removed in the preparation of crêpe. Hence, sheet has a tendency, not encountered in crêpe,<sup>1</sup> to become mouldy on the surface. To overcome this tendency, and at the same time to regularize and hasten the drying of wet sheet, it is usual to dry it in wood smoke.

In order to secure suitable slabs of coagulum, latex intended for the preparation of sheet is coagulated either in (a) pans, or (b) coagulating tanks. Formerly pans were universally used, but tanks have important advantages over pans, and are now replacing them. The pans are usually enamelled vessels of rectangular cross section. Each holds the latex for one sheet only. A common size is 18 in.<sup>2</sup> in length, and 6 in. in width; one gallon of latex being taken for each sheet. When rolled out the coagulum prepared in such a pan is about 9 in. wide, *i. e.* half the width of the packing-cases generally used. On some estates pans of twice the above width are used, in order to secure a sheet equal in width to the width of the packing-cases. (See remarks later on wide sheets.)

*Sheet coagulating tanks.*—In tanks for sheet coagulation latex sufficient for, say, 100 sheets is coagulated in a single vessel; and, by placing boards in the latex, after admixture with acid, while the latex is still liquid, the coagulum is constrained to form as a number of separate slabs. As compared with their position when prepared in pans, the slabs in tanks are formed "edge on";

<sup>1</sup> Except under occasional abnormal circumstances, such as undue thickness accompanied by poor drying conditions.

<sup>2</sup> A length of 22 in., although not usual, has advantages, since the sheet obtained when rolled out fits the packing-cases better than sheet made in 18. in. pans.

that is to say, the depth of latex employed (say, 6 in.) corresponds to the width of the pan.<sup>1</sup> The width of the shallow tanks for sheet coagulation usually corresponds to the length of several (say, three) pans end to end, so that each strip corresponds to a definite number of pan sheets. The strips are usually cut up, after being rolled out, into lengths corresponding to the length of pan sheets.<sup>2</sup>

Sheet tanks are commonly constructed either of brick or reinforced concrete rendered with cement and lined with glazed tiles or of hard wood.<sup>3</sup> The boards employed for dividing the coagulum into slabs or strips are usually of hard wood.<sup>4</sup> The tiles on the sides of the tank may be provided with slots for the reception of the boards. It may be expected that, as time goes on, improvements will be introduced into the construction of sheet tanks.<sup>5</sup>

<sup>1</sup> *Wide sheets in deeper tanks.*—Although the tanks usually used are designed to produce a sheet which when dry is about 9 in. wide, deeper tanks, designed to produce a dry sheet of twice this width, have, it may be pointed out, considerable advantages. (a) They economize floor space. (b) Twice as much latex can be coagulated at once. This is favourable to the preparation of a uniform product. (c) There is a distinct economy in the handling, rolling and packing of a given crop in the form of wide sheet when compared with the labour of handling, rolling and packing it in the form of narrow sheet. (d) Wide sheet preserves its shape during drying better than narrow sheet.

In factories where the rolling machines employed for sheeting are the regular mills used for crêpe preparation, with rolls 15 or 18 in. wide, it is, of course, not possible to make wide sheet. The rolling of sheet does not, however, require machines as heavy as those required for crêping; and the lighter machines built specially for sheet rolling can be obtained with rolls long enough to take 18 in. sheet.

The operation of tanks, using 12 in. depth of latex, and suited to the preparation of wide sheet, which were built at the instance of the writer, was found to be quite practicable. It is recommended that the width of such tanks should correspond to the length of two sheets only. Indeed, it is probably best to construct even the shallower tanks of this width only, as more severe selection, in regard to the smoothness of their surfaces, can be exercised in choosing the division boards; and as, further, the latter, being shorter, are less liable to warp.

<sup>2</sup> In order to obtain ends similar in appearance to those on pan sheets, the strips may be broken up into sheets while in the tank, by placing thin strips of zinc or aluminium between the boards at suitable points.

<sup>3</sup> In the author's experience, the somewhat higher initial cost of the former type of tank is outweighed by greater life and suitability.

<sup>4</sup> The boards should be carefully chosen to have a good surface. Also, it has been found useful to treat the boards with paraffin wax or other material to fill the pores. Wax should not be left on the surface, as it may cause the rubber to stick, but should be completely removed from the surface by fine glass-paper. As the grain tends to come up again when the boards are first put in use, it is necessary to rub them over at intervals, particularly during the first week of their use, with fine glass-paper.

<sup>5</sup> Glass or aluminium have already, with advantage, been employed on one or two estates for lining the tanks.



When using slotted tiles of the type usually supplied (with three slots  $\frac{1}{2}$  in. wide per tile), the distance between the boards, which represents the thickness of latex going to each slab of coagulum, is  $1\frac{1}{2}$  in. Now, in the case of coagulation in the common pans 18 in. long, the thickness of latex going to each slab is  $2\frac{3}{4}$  in. Hence, if the slabs of coagulum prepared in tanks of the usual type are subjected to the same course of rolling as those prepared in pans, the rolling will have a somewhat different effect: the sheet produced will be thinner and will dry more quickly, and probably the proportion of serum substances retained will be different.

Eaton<sup>1</sup> found that, if slabs of coagulum, respectively 3 in. and  $1\frac{1}{2}$  in. thick, were passed through rolls kept at a fixed distance apart, and the resulting sheets were then allowed to air-dry, the sheets from the thinner slabs cured more slowly than the sheets from the thicker slabs. The thickness of the dry sheets from the thick and from the thin slabs differed by about 1 mm., being respectively 3 and 2 mm. In ten experiments the difference in time of cure between the thicker and the thinner sheets was in all cases more than 0.25 hour, and in many cases about 0.5 hour. If, however, the rolls were held further apart for the thin slab than for the thick, so that the sheets from both slabs dried at the same rate and had finally the same thickness (say, 3 mm.), no difference in rate of cure was to be observed.<sup>2</sup>

Eaton suggests, therefore, that, in the interests of uniformity, tank sheet should be rolled less heavily than pan sheet; and, further—in view of the fact, established by his experiments, that the thickness of sheets influences their rate of cure, by, in Eaton's view, influencing the rate of drying and thus maturation—that "all estates should agree to adopt tanks in which the division plates are a similar distance apart." Eaton points out that the lighter rolling which would be called for in order to make its rate of cure the same as that of pan sheet offers the advantage of saving time.

There would, however, seem to be drawbacks to the course recommended by Eaton as compared with the alternative course of increasing the distance between the tank divisions to more

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 214 *et seq.*

<sup>2</sup> It should be pointed out that Eaton's experiments on the comparison of pan sheet with tank sheet were made on unsmoked sheet. In the preparation of smoked sheet factors enter which do not enter in the preparation of unsmoked sheet; and, therefore, it would not seem permissible to apply the results, at all events in a quantitative way, directly to the case of smoked sheet.

than one and a half inches, namely: (a) the softer sheet produced by lighter rolling would tend to lose shape in drying (by sagging) to a greater extent than usual; (b) in cases where a factory is making some of its sheet in tanks and some of it in pans, there would probably always be an element of uncertainty in deciding exactly how much lighter should be the rolling given to the tank sheet.

In the interests of uniformity, it should, in the present writer's opinion, be the aim in each factory to standardize the coagulating procedure in sheet preparation, as regards dilution, thickness, etc., so that the rolling procedure can be standardized to the extent that the distance between the rolls is kept fixed during the rolling of each day's crop.

The preparation of sheet in tanks is more economical of time and labour than its preparation in pans. Tanks have also an advantage over pans in that they facilitate the exact control and supervision of coagulating procedure. Their chief advantage, however, is that they facilitate the achievement of uniformity in the product.

The acetic acid employed for the coagulation of sheet is conveniently used in a concentration of about 1.5 per cent.<sup>1</sup>

*Shrinkage from the division boards.*—Satisfactory sheet can be prepared in a sheet tank only if the strips of coagulum do not stick to the partitions. Preferably the coagulum should shrink away, free, from the partitions, the bottom and the sides of the tank. Shrinkage was found to be dependent to a considerable extent on the dilution of the latex and the concentration of acid added. Working with latex of standard dilution, it was found that, within certain limits, the extent of shrinkage (which could be judged by measuring the amount of separated serum on the following morning) was greater, the larger the amount of acid added. In practice, of course, the extent to which it is advisable to exceed the minimal proportion of acid is limited, not only on

<sup>1</sup> *Sheet skimmings.*—As it is not usual, or, in general, desirable to add sodium bisulphite to the latex employed for sheet, the (crêpe) rubber obtained from the skimmings taken from the sheet pans and tanks after the addition of acid is likely to discolour to a greater or less extent, unless some steps are taken to prevent its doing so. By adding sodium bisulphite in suitable proportion to the skimmed-off latex, a pale colour can be ensured in the crêpe prepared from the latex. Since, however, the latex in question already contains acetic acid when skimmed off, it is necessary to mix sodium bisulphite with it immediately the latex is removed, before it has time to set. This can be done by having sodium bisulphite solution already present in the vessel into which the skimmings are taken. The skimmings and the solution must be mixed without delay.

account of economical reasons, but also by the fact that the setting of the latex must not proceed so rapidly as to make it difficult to get all the partitions in position before the setting begins.

Experience indicated a further conclusion with regard to shrinkage and the achievement of good surfaces on the strips of coagulum, namely: that the latex must be in a perfectly liquid condition, free from any suspicion of being on the point of undergoing natural clotting (cf. p. 174).

*Rolling and ribbing sheet.*—The rolling out of sheet is most efficiently performed by assigning to it a special battery or batteries, each of three smooth-roll machines and one ribbing machine. The slabs of coagulum are passed successively through each of the four machines. The distance between the rolls on each machine is kept fixed, and diminishes from one smooth machine to the next. The object of the ribbing machine is to form ribs on the surfaces of the sheet, in order to expedite drying by increasing the surface and facilitating the draining off of surface water, and in order to make the sheets less liable to stick when packed. Close parallel ribs, such as are produced by rolls cut with rather deep spiral grooves, a quarter of an inch apart, probably represent the most suitable type of ribbing.

*Smoking sheet.*—After superficial water has been allowed to drain off, the wet sheet is hung in specially constructed smoke houses.<sup>1</sup> The rubber is hung in the upper part of the smoke house, the lower part being utilized for the furnaces,<sup>2</sup> in which wood is burnt. In order to prevent dust from the fires getting on to the rubber, the lower part of the house is separated from the upper part by a gauze screen. The temperature in the smoke house is most suitably 110–120° F. The usual thickness of smoked sheet is 2.5–3 mm., or, say, 25–30 g. per 100 cm.<sup>2</sup> of area. Provided that the smoking is kept going with few interruptions, sheet of such thickness is dry within fourteen days.

Smoked sheet is typically translucent and of a bright, rich brown colour. It seems probable that the colour is due chiefly

<sup>1</sup> For notes on the construction of smoke houses, see van Heurn, *Archief*, 1918, 2, 124.

<sup>2</sup> In the author's experience a simple kind of open furnace, made directly accessible from the outside, by sloping the wall of the lower part of the smoke house down to it, or, failing that, a simple open furnace on wheels, which can be withdrawn to the outside for re-charging, etc., is satisfactory. A closed-in furnace, giving a dense and comparatively cool smoke, is not so satisfactory as an open one with a small fire in which rather complete combustion occurs.

to the accelerating influence which the phenolic constituents of the smoke exercise on the activity of the latex oxidase.<sup>1</sup> The depth of colour varies to some extent in different samples of smoked sheet. It has already been remarked that discoloration brought about in rubber by oxidase activity is, so far as is known, without influence on the vulcanizing properties. There is no reason to suppose that in itself the depth of colour in smoked sheet is of any significance in regard to the quality of the rubber. At various periods formerly, however, the market has shown a predilection either for exceptionally dark or for exceptionally pale-smoked sheet. As the ultimate depth of colour in smoked sheet can be adjusted artificially to a considerable extent, it was open to estates, if they thought it worth while, to meet such predilections by making appropriate additions to the latex. Thus, the addition of a small proportion (a smaller proportion than that used in the preparation of pale crêpe) of sodium bisulphite, by retarding oxidase activity, leads to the production of a pale-smoked sheet; the addition of small proportion of phenolic substances,<sup>2</sup> by accelerating oxidase activity, leads to the production of a dark smoked sheet. For several years past, however, it would appear that the market preference has been for a medium depth of colour, such as is obtainable by the normal procedure.

Before proceeding to a consideration of the effect of smoking on the quality of rubber, mention may be made of a number of difficulties relative to the appearance of the sheet. The defects in appearance here in question do not, so far as is known, influence the vulcanizing properties of the rubber in any serious, or, for the most part, in any appreciable degree; but, owing to the circumstance that the broker's valuation of raw rubber samples is largely decided by their external characters, the plantations have felt compelled to devote to these defects an altogether

<sup>1</sup> Whitby, *Rep. Batavia*, 1914, p. 165.

<sup>2</sup> In a patented treatment, known as the Byrne process, wet sheet is subjected for a few hours to the vapour formed by the evaporation and atomization of certain wood products, and, as a result of this exposure the rubber apparently absorbs phenolic substances, which accelerate oxidase activity, with the result that, although the sheet is not dried in smoke but is merely allowed to dry in the air, the sheet when dry is similar in appearance to ordinary smoked sheet.

It is concluded by Campbell and the Imperial Institute (*Dept. Agric. Ceylon Bull.*, No. 27, 1917), that "the process, like ordinary smoking, increases the time of cure." Eaton (*loc. cit.*, p. 267) concludes that "the process offers no special advantages."

disproportionate amount of attention.<sup>1</sup> The chief defects in question are the occurrence of small bubbles in sheet and the occurrence of "rustiness" on the surface of sheet.<sup>2</sup>

#### BUBBLES IN SHEET

The conclusion arrived at by the author in regard to the causes of bubbles in sheet was that in almost every case bubbles can be referred to the decomposition, usually slight, of either the protein or the carbohydrate constituents of the unrolled or of the rolled coagulum. Decomposition giving rise to gas bubbles may occur (a) in the coagulum prior to rolling, *i. e.* while it is standing overnight in the serum, (b) after the coagulum has been rolled.

The formation of bubbles overnight is favoured by insufficient dilution of the latex and the use of a low proportion of acid for coagulation. The formation of bubbles after the rubber has been rolled out is favoured by a slow rate of drying, particularly during the first twenty-four or forty-eight hours following rolling. It appeared that a tendency to bubble-formation arising from the fermentation of the carbohydrate constituents of the latex could often be overcome by dissolving the carbohydrates out of the coagulum to some extent, as, *e. g.*, by flooding the vessels with water soon after the coagulum had formed. It was found, further, that bubbles from this cause were particularly liable to occur in cases where the sheet, after being given a preliminary, light rolling at a sub-station, was transported to a central factory for heavy rolling. From the point of view of avoiding bubbles, it always appeared better to provide an installation of sheet rolling machines at all coagulating stations, so that the sheet could be rolled on the spot.

A very frequent cause of bubbles is the inclusion in the artificially produced coagulum of particles of natural coagulum, owing to premature natural coagulation having set in in the latex before acetic acid was added. The bacterial decomposition of natural coagulum is found to take place more readily than that of coagulum produced artificially by acetic acid.<sup>3</sup> If latex in

<sup>1</sup> It is not suggested here that the plantations should not aim at avoiding the defects here in question. It is suggested, rather, that they have been given an exaggerated importance in the marketing of raw rubber, which has tended to the establishment of false standards of quality.

<sup>2</sup> The term "resinous" has sometimes been employed by brokers to describe rubber showing these defects.

<sup>3</sup> Cf. Whitby, *Agric. Bull. F.M.S.*, 1918, 6, 374.

the state of premature coagulation here in question is used for the preparation of sheet, it is difficult, even when care is taken to make the drying as efficient as possible, to avoid the formation of gas bubbles. When latex is in the very early stage of natural clotting here in question, the particles of natural coagulum present are only very small and usually pass through the sieves. It is not difficult to recognize this state of, as it were, incipient curdling. If a lead pencil or other piece of smooth wood is dipped into the latex and withdrawn, it will be seen that small particles of natural coagulum are adhering to it. When latex is found to be in this state, it is not advisable to use it for sheet-making. The methods of avoiding such a state were discussed in Chapter IV in connection with the collection of latex and the use of anti-coagulants.

Careful attention to all the details that assist in securing rapid and uniform drying of sheet are of importance in overcoming a tendency to bubble formation.<sup>1</sup>

Bubbles arising from the different causes indicated are to a certain extent distinguishable in appearance. Broadly speaking, the following types of bubbles may be distinguished: (a) The bubbles are associated with a pitted surface on the side of the sheet which was undermost in the coagulating pans. Such bubbles are indicative of decomposition having taken place or having started while the coagulum was standing overnight in the coagulating vessel.

<sup>1</sup> Some of the details here in question may be mentioned: (a) It is advantageous to give the wet sheet several hours' air-drying, during the middle of the day, in a position (shaded from the sun by a roof) freely exposed to the air on all sides, before putting it in the smoke house. During this preliminary air-drying, the sheets lose much more water than during an equal period of draining inside the factory. The sheets should be hung wide apart.

(b) In order further to accelerate drying, the use of a "preliminary" smoke house has been found useful. This is a small smoke house, constructed in a rather more open manner than an ordinary smoke house. The sheet is subjected to twenty-four or forty-eight hours' vigorous smoking in this house before being transferred to the main houses.

(c) A definite system of hanging and moving the sheets in the smoke house, aiming at obtaining the most uniform and rapid drying possible, particularly during the first two or three days, is advisable. It has been observed that, in the case of pan sheet, decomposition is most liable to show itself on that side of the sheet which was undermost in the pan. Hence, this side should be placed uppermost when first hanging the sheet.

It is very frequently observed that bubbles are confined to a strip across the middle of the sheet, or are decidedly thicker here than elsewhere in the sheet. This is because, owing to neglect to move the position of the sheets on the supporting wooden rods systematically, a portion of the sheet, which was in contact with the rod, has had less favourable drying opportunities than the remainder. It may be mentioned that, similarly, "rustiness" is often found only on a transverse strip across the middle of the sheet.

(b) Clusters of very small bubbles. The clusters may be apparent only at a few points, or all over the sheet, or confined to a strip across the sheet. When the bubbles are extremely small and close together, they may reflect light in such a way as to give a patchy appearance to the sheet, or to make it appear on casual inspection as though it were not dry. Bubbles of this type are generally indicative of protein decomposition after rolling, particularly of fine particles of natural coagulum, formed by premature natural clotting, included in the sheet.

(c) The bubbles are not clustered, but are discrete, and, as a rule, are larger in size and fewer in number than in the case of type (b). It is thought that they are indicative of carbohydrate decomposition.<sup>1</sup>

Bearing in mind the causes of bubbles, as outlined above, it seems clear, in the light of what is known concerning the various factors involved in the preparation of raw rubber, discussed at different points in this volume, which may influence the vulcanizing properties, that the likelihood of the presence of bubbles being indicative of inferior quality is small. Indeed, in view of the character of the root cause of bubble formation, viz. decomposition of non-caoutchouc constituents of the coagulum, which, at all events in its more pronounced forms, has been shown by Eaton and others to influence the vulcanizing properties of rubber very favourably (cf. Chapter VIII), the presumption is that, speaking broadly, in so far as the causes which lead to bubble formation influence the quality of the product at all, their tendency will be to influence it favourably.

#### "RUSTINESS"

Smoked sheet is said to be "rusty" when, on being stretched, it shows at the point where it is stretched a dull, brown, powdery appearance, reminiscent of a thin film of rust on iron. This condition is due to the presence on the surface of the sheet of a thin film of solid, owing its colour to the smoke, and derived from the latex serum contained in the wet sheet. The film is not visible before the sheet is stretched. Stretching breaks it, and thus makes it noticeable. Speaking broadly, it may be said that the formation of such a film is, like the formation of

<sup>1</sup> A fourth type of bubbles, which is seldom encountered, may be mentioned, viz., large bubbles forming blisters on the surface of the sheet. They arise from over-heating in the smoke house.

bubbles, favoured by conditions which favour bacterial decomposition in the coagulum, particularly by any delay in drying after the sheet has been rolled.

According to Arens,<sup>1</sup> to de Vries and Hellendoorn,<sup>2</sup> and to the present writer's experience, the most generally effective measure against the occurrence of "rust" is rapid surface drying, either by rapid air-drying or by placing the sheet in a vigorously going smoke house after a few hours' dripping.<sup>3</sup> Another measure frequently adopted, and in Eaton's experience<sup>4</sup> most satisfactory, is to wash the surface of the sheets, after the latter have been allowed to drain for a short time, with cold or tepid water,<sup>5</sup> scrubbing if necessary. According to de Vries<sup>6</sup> this measure does not prevent rustiness. Eaton<sup>7</sup> finds in ten experiments that treatment of the rolled sheets with water, even for as long a period as overnight, is without appreciable effect on the vulcanizing properties of the product, and, therefore, concludes that the method of avoiding "rust" by treating the sheets with water is innocuous.

De Vries,<sup>8</sup> however, obtains somewhat different results by soaking freshly rolled sheet in water. He finds that soaking for only half-an-hour reduces the time of cure by 13.45 per cent.; for 1-5 hours by, on the average, 17.5-25 per cent.; overnight (20-24 hours) by 16.0 per cent.; and for 48 hours by only 11.7 per cent. He concludes that two factors are to be distinguished as possibly affecting the result of soaking, namely: an extraction of serum substances, tending to reduce the rate of cure, and an increased degree of maturation,<sup>9</sup> tending to increase the rate of cure. He found that if sheet were kept in water for seven days, its time of cure was reduced by 41 per cent.; becoming almost equal to that of fully matured rubber (cf. Chapter VIII). (In these experiments, the average time of cure of the unsoaked sheet was 93 min.) The thickness of the sheet and the length

<sup>1</sup> *Archief*, 1918, 2, 527.

<sup>2</sup> *Ibid.*, 1917, 1, 197.

<sup>3</sup> The present writer prefers the former of these two measures. Cf. the preliminary air-drying recommended for the prevention of bubbles.

<sup>4</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 300.

<sup>5</sup> The sheets should not be soaked in *hot* water. De Vries and Hellendoorn (*loc. cit.*) find that treatment with water at 60° C. reduces the rate of cure and the viscosity. They confirmed this finding in more extended experiments (*Archief*, 1918, 2, 539) on the influence of hot water on wet sheet. Water at 40° only was without harmful effect on the quality of the product. Vulcanization tests made at an earlier date by the present writer gave results in agreement with those of de Vries and Hellendoorn, as to the harmful effect of hot water on sheet.

<sup>6</sup> *Archief*, 1919, 3, 339.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> *Archief*, 1919, 3, 339.

<sup>9</sup> Presumably due to a reduction in the rate of drying (cf. Chapter VIII).



of the period of soaking will, de Vries supposes, determine which of the two factors will predominate. De Vries supposes that Eaton's experiments the factors happened to compensate each other.

De Vries and Hellendoorn<sup>1</sup> have made some rather extensive observations concerning the influence on the vulcanizing properties of "rust" arising from a number of different circumstances. They find that "rustiness" is in all cases without serious influence on the vulcanizing properties. Any small differences which were to be noticed in their experiments between the rusty sheet and the non-rusty controls could mostly be traced to the circumstances under which the rustiness had been produced, a fact since in practice these circumstances are, as was remarked, of great relation to the formation of bubbles, generally somewhat favourable to decomposition of the non-caoutchouc solids, *i. e.* the maturation, any slight influence which the occurrence of rustiness had on the vulcanizing properties was more likely to be favourable than otherwise.

According to Eaton, the superficial film associated with rustiness consists of dried serum and chiefly of protein. According to Hellendoorn,<sup>2</sup> however, the film does not consist of protein, but "is formed by a jelly-like substance produced from the serum by the action" of aerobic organisms. This, it is stated, has been definitely proved by infection and disinfection experiments.

#### EFFECT OF SMOKING ON QUALITY

Speaking generally, it may be said that smoking wet sheet is without important influence on the vulcanizing properties of the product, but that such effect as it has is probably in most cases unfavourable, although, owing to the fact that more than a single factor is concerned, and that the different factors concerned do not all act in the same sense, its effect is not consistently unfavourable, but may be the reverse. The influence of smoking on rubber has been studied particularly by Eaton and Grantham. In their first investigation<sup>3</sup> smoked sheet was found to cure much more rapidly than comparable samples of unsmoked (air-dried) sheet in twelve out of fourteen experiments. The difference in time of cure was mostly a quarter of an hour, but in some cases

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Vide* De Vries and Hellendoorn, *Archief*, 1918, 2, 527.

<sup>3</sup> *Agric. Bull. F.M.S.*, 1915, 3, 175; *J. Soc. Chem. Ind.*, 1915, 34, 9; *Dept. Agric. F.M.S. Bull.*, No 27, 1918, 173-5.

longer, and in other cases shorter than this period.<sup>1</sup> In two experiments there was no difference in rate of cure between the smoked and unsmoked sheets.

A little later Whitby<sup>2</sup> communicated the results of experiments on the influence of smoking on sheet. He did not observe any important difference between comparable samples of smoked and of unsmoked sheet. In no case was the smoked sample clearly superior, and in several cases it was appreciably inferior in rate of cure; differences in time of cure at 141° in a mix of rubber 100 : sulphur 8 being  $\frac{1}{4}$ – $\frac{1}{8}$  hour. No noticeable differences between smoked and unsmoked sheet in regard to slope, breaking stress or elongation at break were observed.

The only difference between the results of Whitby's investigation and those of Eaton and Grantham's was that the former did not indicate such a *consistent* inferiority in smoked sheet, as compared with unsmoked, as did the latter. This difference is readily explicable in the light of Eaton's subsequent analysis of the smoking process into its different factors.

Eaton distinguishes two opposed effects in the smoking process, namely: (a) its antiseptic effect; (b) its incubating effect. Closely related to these, and largely determining which effect shall predominate, is the thickness of the sheet, as affecting (a) the proportion of serum solids retained by the rubber; (b) the rate of drying. As will appear from the discussion in Chapter VIII, the rate of cure is influenced by the occurrence of bacterial decomposition ("maturation") of the serum constituents (and, it should be added, apart from the occurrence or non-occurrence of bacterial decomposition, by the actual proportion of serum solids present). Hence, on the one hand, by virtue of its antiseptic action, smoking will tend to retard or inhibit maturation of the coagulum, and, on the other hand, by virtue of its temperature, which may be more favourable to bacterial action than the atmospheric temperature, it will probably tend to accelerate maturation. The antiseptic effect will tend to reduce, the incubation effect to increase the rate of cure. In Eaton's words: "The balance of conditions in a smoke house during the first few days of drying determine whether the rubber will vulcanize rapidly or slowly."

<sup>1</sup> In experiments (four in number) by Campbell and the Imperial Institute (*Dept. Agric. Ceylon Bull.*, No. 27, 1916) the effect of smoking on the rate of cure of sheet was found to be much greater than that here mentioned, the time of cure being more than doubled. The number of results given are not numerous (cf., also, the remark *loc. cit.*, p. 21).

<sup>2</sup> *J. Soc. Chem. Ind.*, 1916, 35, 499.

Further, the relative and absolute magnitude of the effects will clearly be influenced by the amount of serum solid, capable of undergoing maturation, contained in the rubber, and by the length of the period during which the rubber retains a water-content sufficiently high to favour bacterial activity, *i. e.* by the rate of drying.

In some experiments on the influence of the thickness of sheet on the effect of smoking, Eaton<sup>1</sup> compared (a) thick slabs, (b) thin slabs, (c) thick sheets, (d) thin sheets. In the preparation of (a) and (b), slabs of coagulum, such as the slabs used for the preparation of sheet, were subjected, not to the comparatively heavy rolling used in the preparation of sheet, but merely to a light rolling by hand. Hence, they retained much more serum than sheet rubber retains, were much thicker and dried much more slowly than sheet;<sup>2</sup> and, as a consequence of these circumstances, maturation was likely to have a much greater effect than in the case of sheet and to produce a rapid-curing rubber. Ten experiments were made. The thickness of the thick slabs ranged in different experiments from 36–12.5 mm., of the thin slabs from 17–5 mm., of the thick sheets from 7.6–3.4 mm., and of the thin sheets from 4.3–3.0 mm. In every experiment the effect of smoking thick slab and thin slab was found to be a retardation of the rate of cure. In most cases the retardation was a quarter of an hour (say, in the case of the thick slab from a time of cure of 1.25 to a time of cure of 1.5 hours, and in the case of the thin slab from a time of cure of 1.5 to one of 1.75 hours), but in some cases it was more and in some cases less. In the case of the thick sheets, the effect of smoking was to retard the cure in seven, to accelerate it in two, and to leave it unchanged in one experiment. In the case of the thin sheets, the effect of smoking was to retard the cure in five experiments and to accelerate it in five.

These results make it appear that the direction of the resultant of the effects which smoking involves is more uncertain the thinner the sheet.

With regard to the two effects, *viz.* the antiseptic effect and the incubation effect, which would appear to be distinguishable in the smoking process, the following experiments relative to their influence when considered separately may be noticed.

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 176.

<sup>2</sup> In order to allow them to complete their drying, they were converted into crêpe after 4–6 weeks, *i. e.* after a period more than sufficient for the completion of maturation.

*The antiseptic effect.*—It has been shown<sup>1</sup> that the introduction of phenols (phenol or cresols) into latex for the preparation of sheet has a clearly marked effect on the vulcanizing properties of the rubber. The addition to latex of 0.35 per cent. of phenol (calculated on the weight of the rubber) lengthened the time of cure, at 141° in the mix rubber 100 : sulphur 8, in one experiment which is quoted, from 2.25 to 2.75 hours and increased the slope from 37 to 39. In further experiments by Eaton and Whitby<sup>2</sup> the retarding effect on the rate of cure of sheet exercised by phenols added to the latex was confirmed. In these experiments the addition of phenol or of cresols to the extent of 0.4 per cent. of the rubber-content extended the time of cure of sheet, at 141° in the mix rubber 90 : sulphur 10, by a quarter of an hour. This quantity did not affect the rate of cure of lightly rolled slab, prepared from latex to which it had been added, and left to mature for one month. Presumably the quantity was too small seriously to interfere with maturation in such slab.

In addition to investigating the effect on sheet of typical phenolic constituents of wood smoke, the above-mentioned authors also investigated the influence of the product of the dry distillation of wood (pyroligneous acid), and of the solution of the water-soluble constituents of wood smoke obtained by bubbling the smoke through water. These materials, which of course contained large quantities of acetic acid, were employed to coagulate latex for the preparation of sheet. Comparable sheets were prepared from the same latex by means of pure acetic acid. It was found that pyroligneous acid had the effect of retarding the cure of sheet by 15–20 minutes. (The effect in the case of lightly rolled slab was a retardation of 5–10 minutes; in the case of crêpe the effect was *nil*.) It appeared, further, that a sample of pyroligneous acid prepared from mangrove wood and richer in phenolic bodies had a more marked effect than a sample prepared from rubber wood and poorer in phenolic bodies. Pyroligneous acid containing wood tar did not differ in its effect from acid freed from tar.

Solutions of the water-soluble constituents of smoke also had the effect of retarding the cure. Their effect was appreciably greater than the effect of pyroligneous acid—a result probably attributable to the greater proportion of aldehyde which they contained.

<sup>1</sup> Whitby, *J. Soc. Chem. Ind.*, 1916, **35**, 497.

<sup>2</sup> *Agric. Bull. F.M.S.*, 1917, **5**, 124; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, 244 *et seq.*

*The incubation effect.*—In experiments with slab rubber, *i. e.* lightly rolled slabs of coagulum, Eaton<sup>1</sup> found in each of ten experiments that slab kept for twelve days in hot air, at the temperature usual in smoke houses, cured more quickly than slab kept for the same period in air at atmospheric temperature; the times of cure being respectively, say, one hour and three quarters of an hour, or, say, one to one and a quarter hours and one hour. Similarly, in each of ten experiments he found<sup>2</sup> ordinary sheet dried in hot air at 120–130° F. to cure more quickly than comparable sheet dried at atmospheric temperature, *i. e.* at about 85° F.

*Direct effect of smoke.*—Further experiments would appear to show that, in addition to the unfavourable effect on the vulcanizing properties which it owes to its indirect action, as a disinfectant, on maturation, smoking has also what may be called a direct (presumably, a chemical) influence unfavourable to the vulcanizing properties.

The bacterial changes (maturation) taking place in wet, lightly rolled slabs, and having as their result the production of rubber, which, owing to the presence of vulcanization catalysts produced by the bacterial action, cures rapidly, reach their limit, so far as their effect on rate of cure is concerned, in a week. At the end of such a period of maturation the rubber has still a high water-content; and, in order to obtain a dry product, it has been customary to convert the slabs into thin crêpe. When such thin crêpe is allowed to dry in the air, the product is found to cure rapidly. Eaton<sup>3</sup> finds, however, that if the product is subjected to the action of smoke its property of curing rapidly is lost, and that it cures only a little more rapidly than ordinary smoked sheet. The effect of smoking slab crêpe in Eaton's experiments was very marked; the time of cure in four typical experiments, belonging to a series of ten, being extended from 1.25 to 2.25, from 1 to 2.5, from 1–1.25 to 2.25, from 1–2 to 2.25 hours. It also appeared that in these experiments an effect of smoking was to reduce the maximal tensile strength which the rubber was capable of developing in vulcanization tests.

It would appear from this investigation that, quite apart from its relation to the bacterial activity which may influence the rate of cure, smoking affects the quality of rubber in a more direct manner. In Eaton's view, "the smoke products themselves either destroy or alter the accelerating agent originally formed, or these

<sup>1</sup> *Loc. cit.*, p. 179.

<sup>2</sup> *Loc. cit.*, p. 182.

<sup>3</sup> *Loc. cit.*, p. 190.

smoke products themselves act as retarding agents and neutralize the accelerating agents formed during the maturation of the coagulum."

*Influence of smoking on crêpe.*—According to experiments by Eaton,<sup>1</sup> the influence of smoke-drying on the vulcanizing properties of rubber in the form of thin crêpe is negligible. This is in accord with the view that in the preparation of crêpe the serum solids are removed almost completely, and, hence, that maturation does not occur.

*Moisture-content of sheet.*—Observations on the moisture-content of sheet have been made by a number of authors.<sup>2</sup> In general the moisture-content of sheet is higher than that of crêpe. This is in accord with its higher content of serum solids. The latter are very hygroscopic. The Delft Institute found the following figures for the moisture-content of samples examined in Holland: 35 samples of smoked sheet ranged from 0.30–1.08 per cent., mean, 0.61 per cent.; 102 samples of crêpe ranged from 0.18–0.90 per cent., mean, 0.42 per cent. De Vries found the following results for the percentage of moisture of samples examined in Java:—

TABLE XLV

		No. of samples.	Mean.	Normal limits.	Highest value.
Latex	{ During wet monsoon .	45	0.67	0.34–1.01	1.37
crêpe	{ „ dry „ .	67	0.59	0.39–0.71	0.95
Smoked	{ During wet monsoon .	92	0.76	0.43–1.07	1.38
sheet	{ „ dry „ .	57	0.87	0.52–1.10	1.20

As in the case of crêpe, so in the case of sheet, the moisture-content varies with the degree of humidity of the atmosphere. But sheet is not so sensitive as crêpe to changes in atmospheric humidity, probably on account of the smaller surface which a given weight presents.<sup>3</sup> In agreement with the conclusion that the retention of moisture by sheet and crêpe is largely determined by the hygroscopicity of the serum solids, it was found<sup>3</sup> that sheet prepared so as to include the whole of the serum solids had

<sup>1</sup> *Loc. cit.*, p. 185.

<sup>2</sup> Krayenhoff van der Leur, *Meded. Delft*, 1916, 473; van Heurn, *Archief*, 1918, 2, 22; de Vries, *Archief*, 1918, 2, 45, 852; Whitby, *J. Soc. Chem. Ind.*, 1918, 37, 278 T.

<sup>3</sup> Whitby, *loc. cit.*

a very high moisture-content, and showed variations of great (absolute) magnitude in its water-content in response to variations in atmospheric humidity. A sample quoted showed at different times moisture-contents ranging from 1.44-3.11 per cent.

De Vries<sup>1</sup> has examined the influence, on the moisture-content of crêpe and of sheet, of the individual factors which may be involved in the preparation of the rubber and which affect the proportion of serum solids left in it. It was found, for example, that dilution of the latex or soaking the coagulum in water led to a reduction in the moisture-content of the product.

#### COMPARISON OF SHEET AND CRÊPE

It is generally recognized<sup>2</sup> that samples of crêpe vulcanize more slowly than comparable samples of sheet. The milling to which the wet coagulum is subjected in the preparation of crêpe has the effect of removing the serum more completely than it is removed in the preparation of sheet; and to this more complete removal is to be ascribed the slower rate of cure of crêpe as compared with sheet. The milling in question appears to be without appreciable influence on any of the vulcanizing properties except the rate of cure (cf. p. 157).

De Vries concludes from the careful comparison of pairs of samples of smoked sheet and crêpe, each pair prepared from the same lot of latex, that the values for maximal tensile strength developed by sheet and by crêpe in vulcanization tests are identical or at the most not more on the average than 0.02 kg./mm.<sup>2</sup> in favour of sheet. In these experiments the average times of cure of sheet and of crêpe were respectively 83 and 109 minutes, *i. e.* the time of cure of crêpe was 31 per cent. greater than the time of cure of sheet. These figures may be taken fairly to represent the relations between ordinary samples of crêpe and of sheet in their rates of cure in a rubber-sulphur testing mix. The following shows the mean results obtained by de Vries<sup>3</sup> in an experiment on the comparison of samples of sheet and crêpe prepared from a given lot of latex. For a comparison of

<sup>1</sup> *Archief*, 1918, 2, 852.

<sup>2</sup> *Vide, e. g.* Eaton, *Dept. Agric. F.M.S. Bull.*, No. 27, 1918; *Dept. Agric. Ceylon Bull's.*, Nos. 23, 24, 1916; Eaton and Whitby, *Agric. Bull. F.M.S.*, 1917, 5, 124; de Vries, *Archief*, 1917, 1, 36, 198; 2, 388, 1919; 3, 267.

<sup>3</sup> *Archief*, 1918, 2, 338, 400.

commercial samples of sheet and crêpe taken at random, see Chapter IX.

TABLE XLVI

	Crêpe.	Smoked sheet.
Thickness (mm.) . . . . .	1.2	3.75
Weight per 100 cm. <sup>2</sup> (g.) . . . . .	5.6	23.4
Moisture (per cent.) . . . . .	0.57	0.73
Ash (per cent.) . . . . .	0.17	0.245
Acetone extract . . . . .	2.72	2.50
Tensile strength (P <sub>B</sub> ) . . . . .	1.39	1.43
Time of cure (mins.) . . . . .	120	90
Slope <sup>1</sup> . . . . .	34	35.5
Index viscosity . . . . .	1.58	1.63

Owing to the fact that the serum is less completely removed from the coagulum in the preparation of sheet than in the preparation of crêpe, the weight of the former produced from a given volume of latex tends to be somewhat greater than the weight of the latter. The influence on the weight of the dry products of circumstances most likely to affect the amount of serum substances retained by the coagulum, viz., the degree of dilution of the latex, the length of the time elapsing between the addition of acid and the milling of the coagulum, soaking the wet rubber in water, have been studied by de Vries and Hellendoorn.<sup>2</sup> They find that, in the typical estate case of 15 per cent. latex allowed to stand overnight, the weight of unsmoked sheet was on the average 0.6 per cent. greater than the weight of thin crêpe yielded by a given volume of latex. If the sheet is smoked, the figure is larger than this.

<sup>1</sup> In other series of experiments (*Archief*, 1917, 1, 36; Chapter IX) the difference in slope between crêpe and sheet was somewhat smaller. It appears that as a rule a difference of about one unit can be expected in the slope of sheet and of crêpe. It may be suggested that the slope of sheet as compared with the slope of crêpe is the resultant of two influences, viz.: maturation, tending to improve, *i. e.* reduce the slope (cf. p. 193); and the phenolic constituents of the smoke, acting in the other direction (cf. p. 181).

As regards index of viscosity, any differences that may exist between crêpe and sheet are only small.

<sup>2</sup> *Archief*, 1918, 2, 361, 393.



## CHAPTER VIII

### MATURATION

It has been shown by Eaton and Grantham<sup>1</sup> that, if, instead of converting it into crêpe or sheet shortly after it has formed, wet coagulum prepared from latex, diluted as usual, is left to stand for several days, rubber which may now be obtained from it will vulcanize with exceptional rapidity: whereas a sample of crêpe prepared by the usual procedure, *i. e.* by crêping the coagulum after it has stood overnight only, will, under the conditions of testing employed by them, require, say, 3.25 hours for its optimum cure, a comparable sample of crêpe prepared by crêping the coagulum after it has stood or "matured" for a week or more will require only, say, 1.25 hours. In a valuable series of investigations Eaton and his co-workers<sup>2</sup> have studied in some detail the maturation of wet coagulum and its bearing on the variation in vulcanizing properties which samples of plantation rubber as ordinarily prepared exhibit (cf. Chapter IX).

The form in which Eaton has mostly prepared rubber for the study of maturation is that given by the following procedure: 1 gallon of latex of a rubber-content of 15 per cent., or a specific gravity of 0.9910, is mixed with 3 oz. of a 5 per cent. solution of acetic acid (0.6 per cent. of acid calculated on the rubber) and allowed to coagulate in an ordinary sheet pan. On the following morning the slab of coagulum is lightly rolled by hand, with a rolling-pin, in order to give it a certain amount of firmness. The exact amount of serum removed by this rolling does not affect the ultimate result, as in any case sufficient is retained by the wet slab for the maturation changes to produce their maximum effect. The wet slab is laid out on suitable supports, and is allowed to remain thus for one week or more. During this period of maturation putrefaction of the proteins in the coagulum takes place: at first the surface becomes slimy and the material stinks con-

<sup>1</sup> *Agric. Bull. F.M.S.*, 1915, **3**, 175; *J. Soc. Chem. Ind.*, 1915, **34**, 989; *J. Soc. Chem. Ind.*, 1916, **35**, 715.

<sup>2</sup> For a collected account of Eaton's investigations, vide *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 398.

siderably; later, a dry crust forms on the surface. The thickness of the slabs varies of course with the heaviness of rolling, but is normally about three-quarters of an inch. At the end of the maturation period, the rubber still contains 20 per cent. or more of water. (A thick piece of rubber of this nature would not naturally lose all its moisture even after keeping for several years.) In order to obtain a dry product, the matured slab is converted into crêpe on the ordinary mills with water running over them. Eaton calls the rubber prepared according to the above procedure slab or slab crêpe.<sup>1</sup>

It has been shown that the period necessary for the completion of maturation, so far as its effect on the rate of cure is concerned, is six to seven days.<sup>2</sup> This is shown by the results of two series of experiments given in Table XLVII (p. 191). Series I in this table refers to slabs of coagulum which were not rolled at all; Series II to slabs slightly rolled according to the usual procedure already described. Slabs of coagula were converted into crêpe after periods of two hours to twelve days, and, as usual in Eaton's work, were vulcanized at 141° in the mix rubber 90 : sulphur 10. The times of cure given in the table are the times required to produce a vulcanizate giving a stress-strain coincident with a standard stress-strain curve.

Eaton and Grantham have shown that the acceleration in the rate of cure which the maturation of wet coagulum produces is dependent upon bacterial (and, possibly, fungoid) activity. This was most conclusively demonstrated by showing that maturation as it affects the rate of cure is greatly retarded by maintaining the wet slab in an ice-chest at 4.5–10° C. instead of at the ordinary atmospheric temperature of, say, 26–31° C. Other means by which the development of rapid-curing properties in slab could be prevented or retarded were as follows: The addition of a large proportion of formaldehyde to the latex, or soaking the freshly-prepared slab in formaldehyde solution; heating the fresh slab (so as to render it partly or wholly sterile); soaking the slab in running water. The influence of these treatments in preventing or retarding the development of rapid-curing properties

<sup>1</sup> The preparation of rubber in this form on a commercial scale is beginning to be taken up on a number of estates. A rubber manufacturing company, which operates a large plantation of its own, has for some four years or more past been preparing rubber for its own use in a substantially similar manner (vide *I.R.J.*, July 21, 1917, p. 15; *Ultée, Archief*, 1917, 1, 70).

<sup>2</sup> Eaton and Grantham, *J. Soc. Chem. Ind.*, 1916, 35, 715.

is clearly in agreement with the view that such development is due to bacterial activity; but, owing to the fact that such treatments may possibly affect the rubber in other ways than in preventing bacterial activity,<sup>1</sup> has less weight in the present connection than has the influence of cold.

Having been led to the conclusion that the occurrence of bacterial changes in wet coagulum has the result of bestowing upon rubber the property of vulcanizing rapidly, and in view of the fact that the bacterial changes significant in this connection were likely to be changes in the latex protein, Eaton and Grantham proceeded to examine the effect of adding serum proteins in their original condition, and after they had undergone bacterial decomposition to ordinary slow-curing crêpe. They separated the heat-coagulable serum proteins. They found that these, added in small amount, had only a slight effect on the rate of vulcanization when in their original form, but that after they had been allowed to undergo putrefaction they had a very marked accelerating effect on the vulcanization. For example: in one experiment the addition of 1 per cent. of decomposed protein reduced the time of cure from 3.5 to 2 hours. They found, further, that casein and peptone were almost without effect on the rate of cure, as judged by tensile tests, when used in their

<sup>1</sup> It may be noted that, as already mentioned (p. 130), de Vries and also Eaton (*loc. cit.*, p. 62) have shown that formaldehyde has a direct (chemical) influence on vulcanization apart from its action, as an antiseptic, on maturation. It should also be noted that Eaton (*loc. cit.*, p. 295) found that, although soaking fresh slab for twenty-four hours in 2 per cent. formaldehyde solution prevented the development of rapid-curing properties, soaking for twenty-four hours in 1 per cent. phenol or in 0.1 per cent. mercuric chloride solution, did not do so to any great extent. Eaton attributes the failure of the two last-mentioned disinfectants to prevent the development of accelerators in the rubber to their action being confined to the surface of the slab. Soaking for twenty-four hours in a saturated solution of boric acid retarded subsequent maturation. The maturation of slab rubber is also retarded by the addition of sodium bisulphite to the latex prior to coagulation (de Vries, *Archief*, 1918, 2, 155). In view of the special relation of formaldehyde to latex coagulation, and to the maturation of rubber coagulum, the special character of the relation of formaldehyde to proteins is worth noting. The addition of formaldehyde to serum-albumin has been found to have the effect of rendering the latter non-coagulable by heat, owing to the formation of methylene-albumin (*vide* particularly Blum, *Zeit. f. physiol. Chem.*, 1896, 22, 127; Schwarz, *ibid.*, 1900, 31, 460. For precipitation reactions: Blum, p. 127, Schwarz, p. 461). Methylene-albumin, in addition to being non-coagulable by heat, is non-precipitable by salts. It has been observed (Whitby, *Plantation Problems of the Next Decade*, Weltervreden, 1914, p. 21) that the addition of formaldehyde to latex inhibits or makes difficult coagulation by heat. And latex to which formaldehyde has been added in considerable quantity behaves abnormally when salts are added to it (Whitby, *Koll. Zeit.*, 1913, 12, 155) and in other ways (cf. pp. 37, 39).

original condition, but had a noticeably accelerating influence when used in a decomposed condition. The effects of decomposed protein in accelerating the cure is very clearly shown by the stress-strain curves which Eaton publishes.

*Isolation of a nitrogenous accelerator from matured rubber.*—It thus appears that during maturation of rubber coagulum a substance or substances are formed, by the decomposition of the protein, which accelerate vulcanization. Stevens<sup>1</sup> has made some experiments with the object of isolating such a substance. The material with which Stevens worked was latex serum which had been kept, in closed bottles, for two to three months.

In the first place the relative potency as vulcanization accelerators<sup>2</sup> of the heat-coagulable proteins from this material, and the solids left in solution after the removal of the heat-coagulable proteins, was determined by examining their effect on the vulcanization of rubber from which almost the whole of the protein normally present had been removed by treatment with benzene (cf. p. 120). Mixes as follows, consisting of rubber 100: sulphur 10, together with the additions mentioned, were cured for three hours at 135°: (1) Original sheet, containing 0.48 per cent. of nitrogen; (2) "protein-free" sheet, containing 0.05 per cent. of nitrogen; (3) sample (2) + 3 per cent. of heat-coagulable proteins from matured serum (nitrogen-content of rubber + addition, 0.57 per cent.); (4) sample (2) + 1.5 per cent. of solids from matured serum after the removal of the heat-coagulable proteins (nitrogen-content of rubber + addition, 0.35 per cent.). The vulcanization coefficients of the vulcanizates were as follows: (1) 3.66, (2) 1.60, (3) 3.08, (4) 5.28.

It will be seen that, although the heat-coagulable proteins accelerate the reaction between sulphur and caoutchouc—replacing in fact a similar amount of protein removed by the benzene treatment—they are by no means as potent as the non-coagulable serum solids. Hence, it would appear that the most potent

<sup>1</sup> *J. Soc. Chem. Ind.*, 1917, **36**, 365.

<sup>2</sup> It has become customary to employ in relation to vulcanization the term "accelerator" instead of the term "catalyst." The organic substances now employed in the rubber industry as accelerators of vulcanization are not so far as is known to be found unchanged at the conclusion of vulcanization; but this circumstance does not, it would seem, imply that they are not to be regarded as true catalysts; for, in the absence of evidence to the contrary, it may be assumed that they are split off from the caoutchouc molecule in an unchanged condition, and that their decomposition is due to side reactions.

accelerating agents produced by the maturation of serum are soluble nitrogenous bodies. In order, if possible, to isolate such bodies, Stevens extracted matured slab rubber with water for several days; precipitated the proteins in the resulting solution by tannic acid; removed the excess of tannic acid by barium hydroxide, and then added phosphotungstic acid to the solution. In this way he obtained in one experiment 0.029 g. of the phosphotungstate of a base (or bases) from 100 g. of rubber. In another experiment, where extraction was done with 2 per cent. sulphuric acid, he obtained 0.032 g. (From pale crêpe he obtained respectively 0.0003 and 0.002 g.) Stevens supposes that the extraction was not complete. In order to examine their effect on vulcanization larger quantities of the base were isolated from samples of matured serum.

It was found that 0.59 per cent. of the base added to a mix of 90 parts of latex crêpe : 10 parts of sulphur had the effect of causing the latex crêpe to vulcanize at about the same rate as matured rubber. Thus, at a cure of one hour at 135°, the crêpe alone gave a vulcanization coefficient of 1.16, whereas with the base it gave a coefficient of 2.69. Two samples of matured slab rubber gave coefficients respectively of 2.73 and 2.42.

In order to obtain the quantity of the base mentioned above, there was required the serum which separated in the coagulating pans from 10 litres of ordinary latex, yielding, say, 1500 g. of rubber. Hence, it appears that the whole of the accelerating substance or agent was not separated. The base separated was, Stevens concluded, somewhat less powerful in accelerating vulcanization than the artificial accelerator, *p*-nitrosodimethylaniline.

The chemical nature of the vulcanization accelerators formed by maturation has not yet been further investigated. Nor have any investigations yet been published on the possibility of directing the maturation (say, by inoculation with suitable bacterial strains), so as to produce the most potent and suitable accelerators. It may be noted that tetramethylenediamine (putrescine), a recognized product of putrefaction, has been found to accelerate vulcanization.<sup>1</sup> Tetrahydropyrrole (pyrrolidine) and guanidines have also been found to act as vulcanization accelerators. Pyrrole and guanidine derivatives have in certain cases been recognized among the products of putrefaction. Leucine was found to have hardly any accelerating effect on

<sup>1</sup> Bayer and Co., *Fr. Pat.*, 464, 533.

vulcanization.<sup>1</sup> Tyrosine, too, does not appear to have much effect.<sup>2</sup>

*Loss of weight during maturation.*—During the maturation process there goes on a large escape of nitrogen—in what form has not been determined—and, further, a considerable amount of the nitrogen present is converted into soluble compounds, which may suffer removal when the wet rubber is crêped;<sup>3</sup> with the result that finally the rubber usually shows a smaller nitrogen-content than ordinary sheet or crêpe<sup>4</sup> (cf. p. 59). The gradual loss of nitrogen, which accompanies maturation as hitherto practised,<sup>5</sup> and which goes hand-in-hand with the development of rapid-curing properties, is well illustrated by the results shown in the following table, which refer to samples allowed to mature for periods of one to twelve days and then crêped.<sup>6</sup>

TABLE XLVII

SERIES I.												
Crêped after (days)	2 hrs.	1	2	3	4	5	6	7	8	9	10	11
Time of cure (hrs.)	3½-3½	3	2½	2½	2	1½	1½-1½	1½-1½	1½-1½	1½	1½	1½
Nitrogen (per cent.)	0.38	0.37	0.30	0.27	0.28	0.21	0.19	0.18	0.19	0.18	0.18	0.17

SERIES II.												
Time of cure (hrs.)	.	3	2½	2½	2	1½	1½	1½	1½	1½	1½	1½
Nitrogen (per cent.)	.	0.42	0.37	0.35	0.21	0.17	0.23	0.23	0.17	0.18	0.17	0.16

The samples crêped two hours or one day after coagulation show the nitrogen-content of ordinary crêpe.

Grantham<sup>7</sup> has studied the distribution of nitrogen between serum and coagulum.

*Maturation of sheet.*—Although in most of the experiments on maturation lightly rolled coagulum retaining a large proportion of serum has been employed, the presence of a large amount

<sup>1</sup> Gorter, *Archief*, 1917, 1, 377. A mix of rubber 92.5 : sulphur 7.5, which, without the addition of leucine, had a time of cure of 115 minutes, cured in 105 minutes when 0.2 per cent. of leucine (calculated on the rubber) was added.

<sup>2</sup> Eaton, *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 319.

<sup>3</sup> Cf. *Dept. Agric. Ceylon Bull's.*, No. 27, 1916, p. 26; No. 36, 1918, p. 13.

<sup>4</sup> Grantham, *Agric. Bull. F.M.S.*, 1915, 4, 1; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, pp. 97-112.

<sup>5</sup> A series of patents (E. M. Slocum and the General Rubber Co., *Brit. Pats.*, 1917; 116,324, 116,326, 116,323, 116,322; *U.S. Pat.*, 1,306,838, June 17, 1919; *Fr. Pat.*, 485,797) appears to contemplate avoidance of loss of nitrogen from maturing wet coagulum by "insolubilizing" the nitrogen by one of a variety of procedures, or by producing an insoluble surface layer which will oppose the escape of nitrogen. Such a layer may, it is claimed, be formed by treating the coagulum with an alcoholic solution of  $\alpha$ -naphthol.

<sup>6</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 108.

<sup>7</sup> *Loc. cit.*

of serum is not in fact essential to the development of rapid-curing properties by maturation. It is necessary to have a certain amount of serum present; for ordinary thin crêpe, even when put under conditions suited to maturation, does not become rapid-curing.<sup>1</sup> But, provided that a small amount of serum is present in the coagulum, the essential requirement for the occurrence of maturation is that the water-content of the rubber shall not fall to a low point during the period of six to seven days necessary for maturation to reach its limit. Hence, for example, if a freshly prepared thin sheet is rolled up, so that it will retain most of its moisture, and is left for six days, it will be found to be noticeably quicker in curing than a comparable sample hung up in the air and allowed to dry in the usual way.<sup>2</sup>

That even during the drying of ordinary sheet, hung up in the ordinary manner in the air, and not rolled up so as to maintain the water-content at an unusually high level, maturation may go on to a certain extent and may influence the rate of cure of the product, is shown by the following experiment.<sup>3</sup> Eleven comparable sheets, from latex containing 1.5 lb. of rubber per gallon, were prepared. One sheet was at once converted into thin crêpe; the remainder were hung to air-dry, and on each subsequent day up to the eleventh day one sheet was converted into crêpe. The samples of crêpe thus obtained had the following times of cure :—

TABLE XLVIII

Sample . . .	A	B	C	D	E	F	G	H	I	J	K
Days . . .	0	1	2	3	4	5	6	7	8	9	10
Time of cure (mins.) .	3½	3	2½	2½-2¾	2½	2½	2½	2½	2¼-2½	2¼-2½	2¼-2½

The progressive change in the rate of cure is best seen by observing the progressive change of position of the stress-strain curve under fixed curing conditions. The curves for a cure of two-and-three-quarter hours are shown in the following figure. It will be observed that the influence of maturation has practically reached its limit after six days.

That maturation is a factor in determining the rate of cure of ordinary sheet, is clearly an important point in the consideration of variation in plantation rubber (cf. p. 208).

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 149.

<sup>2</sup> *Ibid.*, p. 144, *et seq.*; *Dept. Agric. Ceylon Bull's.*, Nos. 26 (1916), 35 (1918).

<sup>3</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 60.

## VULCANIZING PROPERTIES OF MATURED RUBBER

An investigation by de Vries<sup>1</sup> brings out a number of additional points regarding fully-matured rubber. A somewhat striking result observed was the reduction in the slope of the stress-strain curve produced by maturation. In one series of experiments the average slope of matured rubber was 33.9 as against 37.0

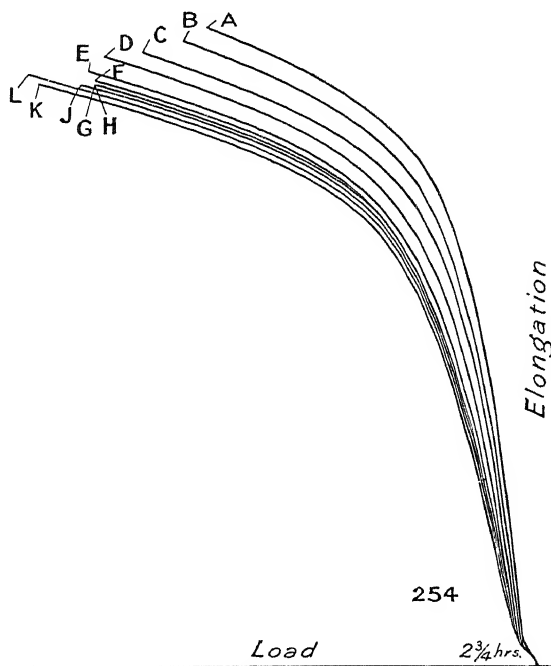


FIG. 34.

for comparable crêpe samples; in other experiments the figures were 33.5 and 36.6.<sup>2</sup>

De Vries concludes that the tensile strength developed in vulcanization tests by fully-matured rubber is only slightly higher than that developed by ordinary crêpe. Following his testing procedure, in one series of experiments the mean tensile strength of matured rubber was found to be 1.37 kg./mm.<sup>2</sup> and

<sup>1</sup> *Archief*, 1918, 2, 213.

<sup>2</sup> A low slope is not a peculiarity of matured rubber, as the present writer found it to be displayed by unmaturing, rapid-curing rubber obtained by the evaporation of latex.



of crêpe 1.35 kg./mm.<sup>2</sup>; in other experiments the figures were 1.44 and 1.40.<sup>1</sup> It is not decided whether this small difference represents an actual difference in the two forms of rubber, or is simply a result of the "sparing" effect of the shorter period of heating required for the vulcanization of matured rubber as compared with crêpe.

As regards the degree of uniformity found in the rate of cure of matured rubber: de Vries states that the rate of cure varies very considerably with the conditions. In his experimental samples it ranged from 50 to 120 minutes, and in samples made on estates from 55 to 100 minutes. Eaton<sup>2</sup> mentions that he found maturation to lead to a remarkable uniformity in rate of cure. A survey of the available data would appear to suggest that under standardized conditions of working different samples of matured rubber may show only comparatively small absolute, but comparatively large relative differences in time of cure. Taking matured rubber as a whole, it would certainly not appear to show a smaller degree of variation than crêpe or even than smoked sheet.<sup>3</sup> On the basis of the data available, it would not be safe to consider that maturation "levels up," as it were, different samples of rubber.

It was found by de Vries that matured rubber derived from natural coagulum had a higher rate of cure than matured rubber derived from acetic acid coagulum. This may be considered as in accord with the greater susceptibility of natural coagulum to bacterial attack as compared with acetic acid coagulum.

*Factors influencing maturation.*—Concerning factors which influence the result of maturation, de Vries came to the following among other conclusions: (1) Dilution of the latex employed leads to slower curing properties. In an experiment, latex with a rubber-content of 25.1 per cent. gave matured rubber curing in fifty minutes, while the same latex diluted to a rubber-content of 7.5 per cent. gave matured rubber curing in eighty minutes. Somewhat curiously, dilution reduced the slope. (2) Keeping the coagulum under water led to a rate of cure almost the same as that of ordinary crêpe; but the slope decreased and took the value for matured rubber. (3) The composition of the latex

<sup>1</sup> Eaton states (*Agric. Bull. F.M.S.*, 1917, 5, 185, 377) that the tensile strength of matured rubber is greater than that of crêpe by 20–25 per cent., but has not published any collation of his vulcanization tests which would substantiate this statement.

<sup>2</sup> *Agric. Bull. F.M.S.*, 1917, 5, 185.

<sup>3</sup> Cf., e.g., a tabulation of results for eighty-one samples, *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 345.

markedly influenced the rate of cure developed by maturation. Thus, abnormal latex, such as may be obtained during the first few days of tapping (cf. p. 209), and which gives ordinary crêpe with an abnormally low rate of cure, was found to yield matured rubber which was, similarly, abnormally slow in curing. (4) The outside layer of the slabs (originally slimy, finally dry and yellow to brown), which is ordinarily washed away during the crêping of matured slab, is without influence on the vulcanizing properties.

*Already-formed accelerators in latex.*—In addition to the vulcanization accelerators which may be formed by maturation, the existence in latex is to be noted of other, already-formed substances, less potent in accelerating vulcanization than the substances formed by maturation, but present in a quantity sufficient, if entirely included in the rubber from a given volume of latex, to bestow on the rubber a rate of cure as high as that usually bestowed on it by maturation. Thus, Eaton and Grantham<sup>1</sup> found that if thin layers of latex were dried *in vacuo* over calcium chloride, the rubber obtained, which had not undergone maturation, but which included the whole of the serum solids, showed a rate of cure similar to that of matured rubber (time of cure, 1.25 hours). In a later experiment<sup>2</sup> it was found that if latex was dried in porous plates the product was not marked by rapid-curing properties. It appeared that the accelerating substance or substances had been largely absorbed by the porous plate. Eaton and Grantham<sup>3</sup> further showed that the water-soluble solids of fresh, unmaturred serum, present after the heat-coagulable proteins had been removed, had a clearly marked accelerating effect on vulcanization. Thus, in one experiment 1.2 per cent. of the serum residue reduced the time of cure from 3.25 to 2.75 hours. In another experiment, employing different percentages of serum solids, results were as follows:—

TABLE XLIX

Percentage of serum residue	0	2	4	6	8	10
Time of cure (hrs.)	2½	2½	2	2	1½	1½

*Types of natural accelerators.*—From the discussion which has preceded in this chapter and in Chapters IV and V, it may be said that vulcanization accelerators as follows have been observed in natural association with caoutchouc:—

(a) The portion of dry rubber which is insoluble in benzene

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, 35, 724.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 79.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1916, 35, 715.

or other rubber solvents. (b) Not improbably substances in the acetone extract of rubber. (c) Substances pre-formed in the latex. (d) Substances formed by maturation of wet rubber.

As to how far the natural accelerators recognized in these different connections form separate and distinct classes, is a question for further investigation.

#### NATURAL AND ARTIFICIAL ACCELERATORS

Inorganic substances, such as, conspicuously, litharge, magnesia and lime, the presence of which accelerates vulcanization, have long been known, and have always been widely used in the manufacture of rubber goods.<sup>1</sup> Within recent years many organic substances which accelerate vulcanization have been brought forward, and are now the subject of eager industrial investigation. The existence of organic accelerators was first signalized in 1912<sup>2</sup> by Hofmann and Gottlob on behalf of the Bayer Company.<sup>3</sup> Piperidine, its homologues and derivatives were the compounds the use of which was proposed. It was stated that a mix of 100 parts of Para rubber and 10 parts of sulphur, which required ordinarily more than one hour for its vulcanization at 53 lb. steam pressure, could be vulcanized perfectly in fifteen minutes if 0.5 parts of piperidine were added.

The impulse to the discovery of the accelerating action of piperidine on vulcanization came from the difficulty which the vulcanization of synthetic caoutchouc offered in the absence of a catalyst. Since 1912 a very large number of organic substances have been found capable of accelerating vulcanization. Indeed, Bayer and Co. have claimed all ammonia derivatives of a basic reaction and all nitrogenous organic bases which possess a dissociation constant greater than  $1 \times 10^{-8}$ . Only an indication

<sup>1</sup> The successful vulcanization of "rubbers" or goloshes by Goodyear would have been impossible but for the use of litharge in the compounds used.

<sup>2</sup> Spence (*J. Ind. Eng. Chem.*, 1918, 10, 115) states that he had recognized the existence of artificial organic accelerators, including piperidine, at a date prior to 1912. He publishes an article on the subject which he prepared in 1911; and he mentions that prior to 1912 he had stated, *inter alia*, in papers in the *Kolloid Zeitschrift*, that vulcanization was essentially a catalytic process.

Van Rossem (*Delft Communics.*, 201) points out that in a patent granted to La Société Geoffroy et Delère in 1903 (*Fr. Pat.*, 1903, No. 329,519) the use of ammonia or of compounds which develop ammonia during vulcanization, as accelerators, was clearly contemplated.

<sup>3</sup> *D.R.P.*, 1912, No. 265, 221.

of the wide range of artificial organic vulcanization accelerators need be given here.<sup>1</sup>

Some of the substances which have found most favour in industrial work are aniline oil, thiocarbanilide, *p*-nitrosodimethylaniline, *p*-phenylenediamine,<sup>2</sup> hexamethylenetetramine. The following list will indicate the character of the substances which have been found effective as organic vulcanization accelerators. It is not exhaustive: (1) Carbon bisulphide addition-products of aniline, dimethylaniline, dimethylamine, etc. (2) Condensation products of aldehydes and ammonia or aniline. (3) A large number of aliphatic and aromatic amines and diamines. (4) Urea, thiourcas, guanidine derivatives. (5) Alkyl derivatives of lead and mercury, sodium and lead oleate.<sup>3</sup>

The possibilities which the use of small proportions of artificial organic accelerators offers of greatly increasing the rate of cure of ordinary sheet and crêpe, and of adjusting it at will, raises the question as to whether it is more advantageous to aim at producing rubber with a high rate of cure, owing to the presence of natural accelerators, or to add artificial organic accelerators to ordinary sheet and crêpe. To attempt to answer this question

<sup>1</sup> For literature on the subject of accelerators, *vide* Ditmar, *Gummi-Ztg.*, 1915, **29**, 424; King, *Met. Chem. Eng.*, 1916, **15**, 231; Spence, *J. Ind. Eng. Chem.*, 1918, **10**, 115; Spence, *J. Soc. Chem. Ind.*, 1917, **36**, 118; Peachey, *ibid.*, 326, 424, 950; Hutin, *Le Caoutchouc*, 1918, 9596; *Le Caoutchouc*, 1916, 8918; *I.R.W.*, 1917, **55**, 190; *ibid.*, **57**, 15; *J. Ind. Eng. Chem.*, 1918, **10**, 865; *I.R.J.*, 1917, 291; Kratz, Flower, and Coolidge, *J. Ind. Eng. Chem.*, 1920, **12**, 317, and numerous patent specifications. In order to obtain positive results with some accelerators, the presence of an inorganic oxide, as an "activator," is necessary.

<sup>2</sup> It is necessary to employ the free base. The hydrochloride is without accelerating effect. This was noted by Eaton (*Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 318). The present writer accidentally confirmed Eaton's observation.

<sup>3</sup> *Action of alkalis*.—Mention may be made of the very powerful accelerating effect of alkalis (Martin, *Rubber Industry*, 1914, 205; Eaton, *Agric. Bull. F.M.S.*, 1915, **4**, 30, 1916; **4**, 162; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, 307). Eaton found that by soaking slow-curing crêpe, with a time of cure of 3.25–3.5 hours, in a 1 per cent. solution of sodium hydroxide for twenty-four hours and then re-washing and re-crêping it, the time of cure was reduced to 0.75–1 hour. Such treatment cannot, however, be employed in practice for the preparation of rapid-curing rubber, as raw rubber treated with alkalis soon becomes sticky and finally liquescent. This last-mentioned fact was first observed by T. Thomson, who states in his *System of Chemistry*, vol. v., Edinburgh, 1807, that a bottle of (raw) rubber filled repeatedly with "ammoniacal gas . . . became soft and then glutinous and never recovered its elasticity. I then tried alkalies in general, and found that they were all capable of producing the same change on caoutchouc."

Scott (*Chem. Met. Eng.*, 1919, **21**, 430) finds the following alkaline substances, added on the mixing rolls in the form of dry powder, to increase the rate of cure, namely: NaOH, Na<sub>2</sub>CO<sub>3</sub>, Ba(OH)<sub>2</sub>, soda lime.

would, in our present state of knowledge, be premature. Although artificial organic accelerators have already come widely into use in industrial practice, few extensive or systematic studies of their influence on vulcanization have yet been published.

Van Iterson and van Rossem,<sup>1</sup> while recognizing the necessity for further study before the question raised above can be answered with any finality, are, nevertheless, inclined to the view that, not only is it more logical, when rapidity of cure is desired, to add artificial accelerators, the amount of which can be controlled, than to rely upon natural accelerators, the nature and amount of which are unknown; but, further, that vulcanization with the aid of artificial accelerators is capable of yielding a product with better mechanical properties than the product yielded by vulcanization with the aid of natural accelerators.

They find that, at a given state of cure, as determined by the position of the stress-strain curve, rubber which has been vulcanized rapidly with the aid of 0.5 per cent. of *p*-nitrosodimethylaniline shows a *longer* stress-strain curve than rubber which has been vulcanized without an organic accelerator; that is to say, that a vulcanizate obtained with the aid of the accelerator in question (or, according to the suggestion of the authors, with the aid of *any* artificial organic accelerators) is capable of being extended further, and, correspondingly, of withstanding a higher stress than a vulcanizate obtained without the aid of an accelerator. In contradistinction to rubber which has been caused to cure rapidly by the addition of an artificial organic accelerator, rubber which cures rapidly on account of the presence of natural accelerators does not, van Iterson and van Rossem point out, appear to show when vulcanized any such favourable behaviour on extension.

The amount of the available data relative to the influence of various artificial organic accelerators on the mechanical properties of vulcanized rubber is, however, very meagre; and, even if the conclusion of the above-mentioned authors regarding the favourable influence of *p*-nitrosodimethylaniline is accepted, it would, in view of the great variety of substances capable of acting as accelerators, be impermissible to assume that all artificial accelerators have a similarly favourable effect. Rather is it to be supposed that different organic accelerators may have different effects on the mechanical properties of the product.<sup>2</sup>

<sup>1</sup> *Meded. Delft*, 1916, p. 116; *Delft Communics*, p. 213.

<sup>2</sup> The following remarks by Spence, implying that different accelerators differ in their effects on the mechanical properties, may be noted: "A

It has been observed<sup>1</sup> that hexamethylenetetramine and condensation product of piperidine and carbon bisulphide<sup>2</sup> have distinctly different effects on the tensile properties of the vulcanizate; the former giving a product more extensible than that produced in the absence of an accelerator, and the latter giving a product very much tougher, *i. e.* showing a much higher maximum tensile strength, but considerably less extension, than the product given in the absence of an accelerator.<sup>3</sup>

Two further results concerning artificial organic accelerators which may be considered as relevant to the present question may be noted :—

Van Rossem<sup>4</sup> found in experiments with a very limited number of rubber samples of different original rates of cure, that the effect of additions of the artificial accelerator "accelerene" (the commercial preparation of *p*-nitrosodimethylaniline) was greater on samples with a lower than on those with a higher rate of cure. His results are shown in the following table.<sup>5</sup> The mix employed was rubber 92.5 : sulphur 7.5; the temperature of vulcanization was 147°.

TABLE L

Sample.	No. 54 T.		No. 26 T.		No. 163 T.		No. 98 T.	
	V.C.	P <sub>B</sub> .	V.C.	P <sub>B</sub> .	V.C.	P <sub>B</sub> .	V.C.	P <sub>B</sub> .
1.5 hrs. without accelerator	1.9	0.55	2.3	0.61	4.2	1.28	5.1	1.43
25 mins. "	0.5	—	0.6	—	1.2	—	1.4	—
" " with $\frac{1}{8}$ " " "accelerene"	1.9	0.30	1.9	0.57	2.1	0.72	1.6	0.71
" " " $\frac{1}{4}$ " " " "	3.1	1.02	3.0	1.04	2.3	0.86	2.5	0.87
" " " $\frac{1}{2}$ " " " "	3.6	1.15	3.6	1.22	2.9	0.96	2.7	1.06
" " " 1 " " " "	4.2	1.10	4.1	1.43	3.3	1.18	3.1	1.11

V.C. = Vulcanization coefficient.

good reagent in this connection must intensify not merely the chemical process of vulcanization, but also the physical; it should toughen the rubber, whether raw or vulcanized, and should render it immune to deterioration. All this has already been achieved in America, and the preparation of rubber far superior to the best natural rubber is now a matter of daily routine; the preparation of a 'noble' rubber, like the 'noble' alloys, has indeed been accomplished."

<sup>1</sup> Unpublished experiments by the author and O. J. Walker.

<sup>2</sup> This product, piperidine-piperidylthiocarbamate, is a very powerful accelerator. One per cent. of it was found to reduce the time of cure in a rubber-sulphur mix to about one-eighth of the time normally required. One per cent. of hexamethylenetetramine reduced the time of cure to about one-third.

<sup>3</sup> See also Cranor, *I.R.W.*, 1919, 61, 137.

<sup>4</sup> *Bijdrage tot de kennis van het Vulcanisatieproces*, Diss., Amsterdam, 1916, p. 180; *Meded. Delft.*, 1916, 111; *Delft Communics.*, 203.

<sup>5</sup> *Bijdrage tot de kennis van het Vulcanisatieproces*, Amsterdam, 1916, p. 181. The data given for these experiments in *Meded. Delft*, 1916, 111, and *Delft Communics.*, 203, are slightly different from those quoted.

It has been stated<sup>1</sup> that better results are obtained in the employment of organic accelerators if, instead of mixing them with the rubber and sulphur in the usual manner, they are treated with sulphur alone, under suitable conditions of temperature, etc., before being mixed with the rubber. It is stated that a reaction-product between the nitrogenous accelerator and sulphur is the agent "which either aids or is entirely responsible for the satisfactory vulcanization of the rubber with sulphur"; and that, as the temperature most suitable for the formation of such a reaction-product is only occasionally and by mere coincidence the temperature employed in vulcanization, it is more rational and satisfactory to prepare the reaction-product as a separate step prior to vulcanization. If this contention is well founded, it certainly tells in favour of the employment of artificial accelerators as against accelerators naturally included in the rubber.

<sup>1</sup> *Brit. Pat.*, 1919, No. 130,857 (North British Rubber Co., Goodyear Tyre and Rubber Co.), (*I.R.J.*, 1919, Sept. 13, 477).

## CHAPTER IX

### VARIATION

*Comparison of Brazilian and plantation rubber.*—Prior to the advent of plantation rubber, the most important rubber sort available to the rubber manufacturing industry was the rubber, prepared from wild trees of *Hevea brasiliensis* in the region of the Amazons, known as Fine Hard Para. In the preparation of Fine Hard Para, undiluted latex, in very thin layers, obtained by dipping a paddle into the latex or by pouring latex over a paddle or over a part of a pole, is subjected to the action of smoke.<sup>1</sup> Layers are superimposed until a large mass is built up.

The experience of the rubber manufacturing industry with Fine Hard Para has been a long one; and, naturally, this grade of rubber has in some measure assumed the position of a standard in regard to discussions concerning the quality of plantation rubber. It is generally conceded that the chief defect of plantation rubber now put on the market, when considered as a whole and compared with Fine Hard Para similarly considered, is its lack of uniformity—perhaps particularly in respect of rate of cure.<sup>2</sup>

Before proceeding to a comparison of Fine Hard Para and plantation rubbers in regard to their degree of uniformity in vulcanizing properties, it should be pointed out that the method of preparation followed in making Fine Hard Para appears to have no advantages from the point of view of the quality of the

<sup>1</sup> The nut of *Attalea excelsis* (Urucuri nut), which, it is stated, is favoured in Brazil as a fuel (in combination with wood) for the production of smoke for the coagulation of latex, has been subjected to examination by Frank and Grädinger (*Gummi-Ztg.*, 1910, 1328). They found that the woody portion of the nuts gave on distillation a tar and an aqueous distillate which did not differ greatly in composition from the corresponding products of beech wood. In the tar was found methylpyrogallol, cocculignol, cresol, guaiacol, mono-pyrocatechol, a sesquiterpene and pyridine derivatives. In the aqueous distillate was found large quantities of formaldehyde and of acetone, and in addition xanthogallin, homo-pyrocatechol, formic, acetic and propionic acids.

<sup>2</sup> Complaints are sometimes made in factories manufacturing rubber goods about the alleged deficiency of plantation rubber in certain qualities, which it is difficult to define with exactness, but the absence of which in the dough or in cements renders the "making-up" of rubber goods less easy than is the case in their presence.



rubber produced, as judged by ordinary vulcanization tests, over the plantation methods of preparation. This is rendered very probable by an examination of the results given by average samples of Fine Hard Para and of plantation rubbers under the same testing conditions,<sup>1</sup> and particularly by the results of some strictly comparative tests in which the two methods (the Brazilian and the plantation) were applied to the same lot of latex.<sup>2</sup>

The results of applying the Brazilian procedure and the plantation procedure followed in making smoked sheet to the same lot of (plantation) latex gave products which in vulcanization tests, in the mix rubber 100 : sulphur 8 cured at 141°, showed the following results:—

TABLE LI

	Brazilian procedure.	Smoked sheet procedure.
Rate of cure (hrs.) . . .	2·5	1·75
Slope . . . . .	40	38
P <sub>B</sub> (lb./in. <sup>2</sup> ) × L <sub>B</sub> . . .	2411 × 1029	2264 × 1028

The smoked sheet here appears as somewhat better than the Brazilian sample: the breaking figures for the two samples are similar,<sup>3</sup> but the slope of the stress-strain curve and the rate of cure are better in the case of the smoked sheet. The latex from which the above samples were made was from young trees (five-year-old trees).

Samples were also made from the latex of older trees (fifteen years old). In this case, in order to build up a larger mass of Fine Hard Para, the Brazilian operation was conducted on four days. On each day a sample of smoked sheet was prepared from the latex employed. The results of the vulcanization tests are shown in the following table:—

TABLE LII

	Brazilian rubber.	Mean of smoked sheets. <sup>4</sup>
Rate of cure (hrs.) . . .	2·5	2·5
Slope . . . . .	38	36
P <sub>B</sub> (lb./in. <sup>2</sup> ) × L <sub>B</sub> . . .	2137 × 1019	2192 × 1044

<sup>1</sup> *Viðe, e. g. Dept. Agric. Ceylon Bull., No. 23, 1916, p. 16; Dept. Agric. F.M.S. Bull., No. 27, 1918; Delft Communics.*

<sup>2</sup> Whitby, *J. Soc. Chem. Ind.*, 1916, 35, 493.

<sup>3</sup> As only one test piece was examined, the difference in breaking stress between the samples is within the experimental error.

<sup>4</sup> In the four individual samples the rate of cure ranged from 2½ to 2½ hours; the slope was constant.

In this case the rubber prepared according to the Brazilian procedure appears as equal in rate of cure to the smoked sheet and inferior only in the slope of the stress-strain curve.<sup>1</sup>

Forms of apparatus which aim at preparing rubber by the smoke coagulation of thin films on the Brazilian plan, in a manner applicable to plantation work, have been brought forward from time to time, but have not recommended themselves. Their rate of output is in all cases too low to make their employment feasible for the preparation of the large crops of rubber with which the plantations have to deal. And it has now received general recognition that the solution of any defects, which the present methods of plantation preparation may involve, is not to be sought in the direction of substituting for those methods an imitation or modification of the Brazilian method.

*Degree of variation of Fine Hard Para.*—Eaton<sup>2</sup> found that the time of cure of twenty-six samples of Fine Hard Para received over a period of about two years ranged only from two and a half to three hours. The Delft Institute<sup>3</sup> found that the vulcanization coefficient of nine samples of Fine Hard Para cured under the same conditions, viz. for one and a half hours at 147° in the mix rubber 92.5 : sulphur 7.5, ranged from 2.67 to 3.81—a smaller range than plantation rubber, according to their tests, would have been likely to show.

Eaton<sup>4</sup> suggests that the comparative uniformity exhibited by Fine Hard Para samples in their rate of cure is probably attributable, not to any intrinsic character of the Brazilian smoking process, but merely to the circumstance that, since each mass of Fine Hard Para is built up by working on a number of days, variations which may affect rubber prepared on different days are largely neutralized.

In view of the fact that Fine Hard Para includes a large proportion of the serum solids, which, as has already been pointed out, are vulcanization accelerators, it might perhaps have been expected to cure with marked rapidity; whereas, in fact, its rate of cure is approximately that of average samples of smoked sheet—a form of rubber which contain only a small proportion of the

<sup>1</sup> Not improbably the unfavourable effect of the Brazilian procedure on the slope, which appears in these tests, is attributable to the influence of the comparatively high proportion of phenolic substances which the Brazilian rubber includes. It appeared in other experiments (Whitby, *loc. cit.*) that the addition of phenols to latex has a noticeable influence on the slope of the stress-strain curve.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 364.

<sup>3</sup> *Delft Commun.*, p. 170. <sup>4</sup> *Loc. cit.*, p. 363.

serum solids. The failure of Fine Hard Para to show as high a rate of cure as might have been anticipated is probably attributable largely to the unfavourable effect on the rate of cure of the smoke products—particularly phenols and formaldehyde—associated with it (cf. p. 181). It is also not improbable that the age of the trees tapped on the Amazon, which is very great when compared with that of most of the plantation trees, influences the rate of cure in the direction of diminishing it (cf. p. 210).

#### DEGREE OF VARIATION IN PLANTATION RUBBER

That differences of form—as sheet, crêpe, slab<sup>1</sup>—cause variation in plantation rubber considered as a whole, is sufficiently clear from what has gone before. But, apart from such variation, there is considerable variation in the commercial product, prepared, on a large number of different estates, in any one form. In all probability the degree of variation was greater five or six years ago than it is to-day; but it is still very considerable. The following data on the amount of variation observed in collections of plantation rubber samples which have been subjected to vulcanization tests by various workers may be noticed.

A collection of samples, apparently mostly prepared in Java in 1914, was examined by the Delft Institute. Each sample was vulcanized for one and a half hours at 147° in the mix rubber 92.5 : sulphur 7.5. The results have been treated statistically by van Rossem.<sup>2</sup> In the following table are shown the frequency tables for the vulcanization coefficients of: I, all the samples, 456 in number; II, 236 samples of latex crêpe; III, 105 samples of sheet.

TABLE LIII

Vulcn. coeff.	1'45-1'95	1'95-2'45	2'45-2'95	2'95-3'45	3'45-3'95	3'95-4'45	4'45-4'95	4'95-5'45	5'45-5'95
I .	15	57	87.5	96.5	87	61.5	32.5	13	6
II .	7	39	52	61	46	24.5	5.5	1	0
III .	4	5	12.5	9.5	20	26	16	9	3

<sup>1</sup> *Block rubber*.—Mention may be made of "block" rubber. This is produced only to a very small extent. It is prepared by drying thin crêpe in a vacuum or hot-air drier, and then pressing the still-warm rubber together in a hydraulic press. It is essentially similar in its vulcanizing properties to thin crêpe (*Dept. Agric. F.M.S. Bull.*, No. 27, 1918, 259; *Dept. Agric. Ceylon Bull.*, No. 27, 1916, 27).

<sup>2</sup> "Bijdrage tot de kennis van het vulcanisatieproces," Diss., Amsterdam, 1916; *vide also Delft Communics.*

The samples in each collection show a normal distribution.

The vulcanization coefficient may be taken as indicating the rate of cure. It may be noticed that this table brings out the higher rate of cure of sheet as compared with crêpe; for, whereas the medial vulcanization coefficient for crêpe is seen to be 2.95-3.45, that for sheet is seen to be 3.95-4.45.

In a collection of 223 samples of smoked sheet prepared in Malaya, some of them by special or experimental processes, Eaton<sup>1</sup> found the rate of cure to range from one and a half to three and three-quarter hours. The majority of the samples cured in from two and a quarter to three hours. Eaton remarks that, since the date at which these samples were collected, the adoption of more uniform methods on estates has considerably reduced the variation likely to be found. In addition to variation in rate of cure, the samples showed some variation, which, however, was relatively smaller in extent, in tensile properties. In a collection of ninety-seven samples of latex crêpe the same author found the optimum time of cure to vary from two to three and a half hours.

De Vries and Spoon<sup>2</sup> have published an analytical survey, in regard to variation, of the results of vulcanization tests on a considerable number of samples prepared on estates in Java in 1917 and 1918. The number of samples examined was as follows:—Smoked sheets: in 1917, 295 samples derived from fifty-five estates; in 1918, 193 samples derived from forty-two estates; Latex crêpe: in 1917, 265 samples derived from thirty-two estates; in 1918, 131 samples derived from twenty-four estates. The results of this survey may be considered in some detail.

*Variation in tensile strength.*—The mean values and the normal range of values are shown in the following table.

TABLE LIV

	Mean.	Normal range.
Smoked sheet, 1917 . . .	1.405	1.36-1.45
„ „ 1918 . . .	1.377	1.34-1.41
Crêpe, 1917 . . .	1.385	1.34-1.42
„ 1918 . . .	1.372	1.34-1.40

The small decrease in the figures for sheet in 1918 as compared with 1917 was chiefly caused by the inclusion in the year's samples

<sup>1</sup> *Loc. cit.*, p. 324 *et seq.*

<sup>2</sup> *Archief*, 1919, 3, 246.

of rubber from young estates recently come into tapping. The mean figures given by these collections of samples are in fair accord with the conclusion, deduced from tests on strictly comparable samples (cf. p. 184), that whether rubber is prepared in the form of sheet or in the form of crêpe is practically without influence on the tensile strength shown on vulcanization.

As already indicated, the greatest amount of variation in plantation rubber is met with in the rate of cure, but a noticeable degree of variation in the maximal tensile strength which individual samples are capable of developing on vulcanization appears by no means to be lacking; although there does not appear to be, in regard to tensile strength, any evidence, such as there is in regard to rate of cure, that the degree of variation of plantation rubber is greater than that of Fine Hard Para. Further: as de Vries and Spoon point out, tensile strength (and also slope) must, at all events, in the present state of our knowledge, be regarded as a more fundamental property than rate of cure, since the latter is, as it were, accidental, and can be adjusted at will by adjustment of the proportion of natural or artificial accelerator associated with the rubber, whereas the former appears to be intrinsic; deficiencies in it being irremedial.

De Vries and Spoon find that the rubber from some estates consistently gives figures for tensile strength which are below the normal level. And they believe that in such cases a somewhat inferior tensile strength is an innate character of the rubber. The following table shows the results which they found for the rubber of a number of estates preparing crêpe.

TABLE LV

1917.				1918.		
No.	No. of samples.	Mean.	Limits.	No. of samples.	Mean.	Limits.
1	12	1'40	1'37-1'45	12	1'39	1'34-1'46
2	12	1'39	1'32-1'46	12	1'38	1'33-1'44
3	13	1'395	1'33-1'45	12	1'39	1'37-1'47
4	11	1'36	1'31-1'44	12	1'38	1'35-1'42
5	10	1'375	1'32-1'49	12	1'365	1'31-1'41
6	6	1'42	1'37-1'45	12	1'36	1'30-1'43
7	10	1'41	1'35-1'47	12	1'355	1'28-1'40
8	12	1'385	1'27-1'46	12	1'36	1'34-1'42
9	7	1'34	1'30-1'38	6	1'37	1'30-1'41
10	15	1'34	1'22-1'45	8	1'32	1'26-1'39
11				30	1'33	1'27-1'40
12				20	1'29	1'24-1'36

Compared with the average figures mentioned above, Estates 1-3 show good average figures and seldom produce samples below the average; Estates 6-8 have, on the whole, a normal tensile strength; but Estates 9-12, and among them a well-known, old estate, give low figures throughout. The causes leading to a tensile strength consistently somewhat low in the product of a given estate doubtless lie in considerations of soil, climate or hereditary factors (strain of seed), the effects of which it would be difficult to eliminate. Hence, a uniform, high tensile strength from all estates is to be regarded, at all events in the present state of our knowledge, as unattainable.

*Variation in slope.*—The average figures for slope were as follows:—Smoked sheet: 1917, 37.2; 1918, 36.5; crêpe: 1917, 35.95; 1918, 35.5. As in the case of the comparative tests previously mentioned (p. 184), smoked sheet appears to have a somewhat greater, *i. e.* somewhat poorer slope than crêpe. The variation in slope observed was not very great. Nearly all the samples fell between 34 and 39, the ordinary figures for smoked sheet being 36-38, and for crêpe 35-37. Whether the differences observed are of any practical importance requires further investigation. Large variations in slope are found normally only in the lower grades.

*Variation in viscosity.*—Variation in the figures for the "index of viscosity" was large. The range was roughly from 1.3 to 2.0, and the mean figure both for smoked sheet and for crêpe 1.64. A large variation in this property was to be expected, as the figure is influenced by so many factors. The fluctuations in viscosity did not coincide with the fluctuations in rate of cure.

*Variation in rate of cure.*—The results obtained regarding the rate of cure are summarized in the following table. The times of cure in minutes under de Vries' conditions of testing are shown.

TABLE LVI

	Mean.	Average deviation from mean (per cent.).	Normal range.	Limits.
Smoked sheet, 1917	99	9.9	85-105	65-140
" " 1918	96	10.5	85-105	65-130
Crêpe, 1917 . .	119	7.3	110-125	70-150
" 1918 . .	118	5.1	110-125	85-130

It will be seen that in 1917 smoked sheet cured in 83 per cent. and in 1918 in 81 per cent. of the time required for crêpe. From

these observations and various experiments de Vries concludes that under the conditions of testing employed by him smoked sheet has a time of cure on the average twenty minutes and unsmoked sheet twenty-nine minutes less than crêpe.

It is noteworthy, however, that although having a shorter time of cure, smoked sheet is more variable in its time of cure than crêpe, as may be seen from the column, "Average deviation from the mean." De Vries and Spoon conclude that smoked sheet shows a degree of variation one and a half to two times as great as crêpe. A greater degree of variation in rate of cure for smoked sheet as against crêpe is also the experience of Eaton.

A survey by Schidrowitz and Goldsbrough<sup>1</sup> of the results obtained on subjecting some 500 samples of different grades prepared on seven different plantations during 1915 and 1916 provides further data on the extent of variation of commercial samples of plantation rubber. The survey agrees with de Vries and Spoon's conclusion that (brown) crêpes of the lower grades show, comparatively, greater variation in slope than the latex grade. It shows also that on the average the lower grades are inferior to latex rubber in slope and tensile strength.

#### FACTORS PRODUCING VARIATION

What has been said in the chapters on the preparation of crêpe and of sheet will have indicated the nature of the factors that, during the course of its preparation, may possibly influence the vulcanizing properties of the product. Assuming that acetic acid is the only coagulant in question, factors which during its preparation may influence the quality of the rubber are, broadly, (a) factors which influence the proportion of serum substances retained by the rubber; (b) factors which influence the maturation of such substances. The factors which are most likely to vary in the ordinary conduct of plantation work are probably: (1) the degree of dilution of the latex; (2) the thickness of the coagulum and the extent to which it is rolled; (3) the rate of drying; (4) the smoking conditions.

It is, however, necessary to recognize that, in addition to factors in variation which are associated with the preparation procedure, there is a group of what may be termed physiological factors which have entered in before the preparation of the rubber from the latex has been put in hand; so that, despite the employ-

<sup>1</sup> *I.R.J.*, 1917, 54, 162, 184.

ment of a strictly uniform method of preparation, the rubber from one group of trees may differ considerably from the rubber from another group. In the first experiments<sup>1</sup> relative to the existence of physiological factors in variation, it was found that smoked sheet prepared according to a uniform procedure from time to time from different areas, while almost constant in properties from a given area, might differ noticeably from one area to another. Distinct differences in the rate of cure and in the slope were observed. The data were not sufficient to decide whether there were differences in tensile strength. De Vries has since made a number of valuable investigations into the physiological factors involved in variation. His main results are as follows:—

(a) *Constancy in properties of the rubber from one group of trees.*—As indicating that the vulcanizing properties of rubber prepared on different occasions in a uniform manner from even as small a group as 150 trees are constant, the following data may be noticed:—Over a period of five months samples of rubber were prepared on from four to eight occasions during each month from a given group of 150 trees. In all except seven of the thirty-four samples the time of cure was 130–135 minutes; in three samples it was 125; in two 140; and in two 120 minutes. (The error of determination is nearly five minutes.)<sup>2</sup>

De Vries concludes from his investigations that “one of the chief causes of differences in first quality plantation rubber is the fact that practically any group or combination of trees produces rubber of somewhat different properties, notably different in rate of cure. Separate divisions or fields of an estate all give a rubber with a special but for that group fairly constant rate of cure.”

(b) *Opening a new cut.*—De Vries has observed repeatedly that the latex given during the first week or two by a new tapping cut and the rubber obtained from such latex are distinctly abnormal. The latex has an abnormally high rubber-content; the rubber is characterized by an exceptionally slow rate of cure. Also, the slope is exceptionally low (*i. e.* good). As tapping is continued, the rate of cure and the slope gradually change to figures normal for the group of trees in question. The anomalous condition does not disappear immediately wound response, as judged by the yield of rubber, has established itself, but lasts for some time longer. With the changes in the rate of cure and slope changes in the viscosity also occur. The viscosity becomes smaller.

<sup>1</sup> Whitby, *J. Soc. Chem. Ind.*, 1916, **35**, 493.

<sup>2</sup> *Archief*, 1917, **1**, 280.



Later, after, say, two to three months, the viscosity was observed to increase again.

One hundred and fifty trees, the normal time of cure for the rubber from which was, as mentioned under (a), 130-135 minutes, showed when first tapped a time of cure of 180 minutes, and reached the normal time only after two to three weeks.<sup>1</sup> In another case<sup>2</sup> the rubber from a group of sixteen trees showed on the second day of tapping a time of cure of 145 minutes; and the time of cure had fallen to a constant, normal value of 100 minutes only three to four weeks later.

(c) *The tapping system*.—A heavier tapping system as compared with a lighter one leads to a greater rapidity of cure. (It also leads to a lower rubber-content in the latex.) Indeed, de Vries concludes that any circumstance connected with the tapping which put a heavier "stress" on the trees leads to an increase in the rate of cure, and, conversely, that any circumstance connected with the tapping that reduces the stress put upon the trees leads to a slower rate of cure. Thus, a group of 159 trees being tapped by one cut on half the circumference showed—after an initial, abnormal period, such as that mentioned under (b)—an average time of cure of 135 minutes. When a second cut on half the circumference was also tapped, the average rate of cure—after an initial, abnormal period—was 119 minutes.<sup>3</sup> It appears, too, that under heavier tapping trees get over the abnormal period which follows the opening of a cut more rapidly than under lighter tapping.

Circumstances other than a change in the severity of tapping under which a change in the "stress" put on the tree changes the vulcanizing properties of the rubber, are the following: (1) Seasonal change in the yield. In an experiment de Vries found the trees to give 8.5 g. of rubber per diem during March and April, and 13 g. during December and January, and that, correspondingly, the rubber during these periods cured in 111 and 105 minutes. (2) Interruptions in regular daily tapping. (3) Shallow tapping. (4) Pollarding. This acts as a greater stress. When trees were continued in tapping after being pollarded, the rate of cure increased at once. Before pollarding the time of cure in an experiment<sup>4</sup> was  $> 100$  minutes; after pollarding it was  $< 95$  minutes.

(d) *Age of the trees*.—It is hardly possible to determine the

<sup>1</sup> *Loc. cit.*, 263.

<sup>3</sup> *Ibid.*, 1917, 1, 266-7.

<sup>2</sup> *Archief*, 1918, 2, 252.

<sup>4</sup> *Ibid.*, 1918, 2, 241.

influence, if any, of the age of the trees on the vulcanizing properties of the rubber by simple, direct experiments. By means of a careful collection and collation of material, de Vries<sup>1</sup> has, however, been able to formulate the following conclusions relative to the question. The limits of age of the trees to which the material referred were four and *ca.* forty years.

(1) The tensile strength for older trees is not appreciably better than for younger trees. (In the case of certain young trees, which had been tapped for only a short time, a lower tensile strength was found, without, however, its being attributable with certainty to the youth of the trees.<sup>2</sup>) (2) The slope of the stress-strain curve is in most cases the same, but is sometimes better for old trees. (3) The rate of cure diminishes very appreciably with the age of the trees. The oldest trees in Java (35 and 40 years old) gave the slowest-curing rubber examined. The extreme figures for rate of cure in any of de Vries' tables are in a case where trees 35 years old show a time of cure of 145 minutes, and trees eight years old of 110 minutes. In other tables are such figures as 110 minutes for five-year-old and 125 minutes for ten-year-old trees, or, again, 120-125 minutes for seven-year-old trees, and 130 minutes for 18-34-year-old trees. (4) The viscosity with old trees is nearly always above, and that with very young trees below the average.<sup>3</sup>

It thus appears that increasing age in the trees leads to a slower rate of cure and does not clearly improve any of the other vulcanizing properties.

(c) *Lower and upper cuts.*—A group of trees was being tapped by two quarter circumferential cuts, one above the other, at heights of 70 and 120 cm. When the latex from the two cuts was collected separately, the rubber from the two cuts was found to be practically identical. The only difference indicated was a very slightly greater rate of cure in the latex from the upper cut. The experiment covered a period of nineteen months.

(f) *Changing the tapping surface.*—In view of the fact that the opening of a new cut had been found, as stated above, to produce anomalies in the latex, and that the latex at first obtained from a new tapping surface on trees in continuous tapping

<sup>1</sup> *Archief*, 1917, 1, 169.

<sup>2</sup> In so far as commercial samples of rubber produced by young estates are inferior to those produced by older estates, the inferiority is most likely due to inexperience and unsatisfactory equipment.

<sup>3</sup> Additional data relative to the question as to whether old trees give better rubber than young ones are to be found in *Dept. Agric. Ceylon Bull.*, No. 27, 1916, p. 14; Whitby, *J. Soc. Chem. Ind.*, 1916, 35, 493.

often shows some of the phenomena which accompany the opening of a new cut, viz. a tendency to oxidative (purple) discoloration or to a yellow colour in the latex, it was not improbable that changing to a new tapping surface in the regular course of tapping would also produce anomalies in the latex. Experiment shows, however, that it did not do so to any appreciable extent.<sup>1</sup>

It would thus appear that, when a tree is in regular tapping, so that its laticiferous system considered as a whole has not had a period of rest, the opening of new cuts does not affect the vulcanizing properties of the rubber. Hence, a change of tapping surface in ordinary estate routine is not a factor in producing variation. It is of interest to note here that a yellow colour in the rubber, when arising from a change of tapping surface, is without significance so far as vulcanizing properties are concerned.

*Generalization concerning physiological factors in variation.*—It appears possible to make (though de Vries himself has not done so), on the basis of the results just stated, concerning physiological factors in variation, a generalization to the effect that, conditions leading to a higher rubber-content in the latex tend to reduce, and, conversely, that conditions leading to a lower rubber-content in the latex tend to increase the rate of cure of the rubber. Under each of the conditions mentioned above in which a change in the rate of cure was observed, a change in the rubber-content of the latex in the sense indicated by the above generalization was also observed.

Further, the suggestion may be hazarded that the changes observed in the rate of cure are dependent upon changes in the ratio (rubber/serum-solids) in the latex. For de Vries has shown<sup>2</sup> that, no matter how widely the specific gravity of latex may vary, the specific gravity of the serum remains almost constant. Now, any increase in the "stress" put on the tree leads, according to de Vries, to increase in the specific gravity, and, correspondingly, to a decrease in the rubber-content of the latex; any lightening of the stress leads to an increase in the rubber-content of the latex. But neither change is accompanied by any important change in the percentage of solid matter in the serum; although, it should be mentioned, a heavier stress increased from  $< \frac{1}{7}$  to  $> \frac{1}{5}$  the proportion of mineral matter in the serum.

The connection just stated between the stress on the tree and the character of the latex and of the serum was shown particu-

<sup>1</sup> *Archief*, 1919, 3, 130.

<sup>2</sup> *Ibid.*, 1919, 3, 183; cf. p. 138.

larly for the following cases, namely: (a) recommencement of tapping after a period of rest; (b) light and heavy tapping systems; (c) pollarding; (d) periods of rest; (e) shallow tapping. Also, it is well known that the rubber-content of latex increases with the age of the tree.<sup>1</sup>

Hence, it appears that it may be stated generally that an increase in the ratio (serum-substances/rubber) leads to a higher and a decrease in the ratio to a lower rate of cure. This conclusion, it may be noted, is in accord with that which an examination of the factors in variation involved in the preparation procedure would suggest, viz. that increase in the amount of serum substances associated with the rubber is favourable to rapidity of cure.

#### THE ACHIEVEMENT OF UNIFORMITY

In order to avoid, in the vulcanizing properties of the product prepared in any one form, such variation as arises from variation in the details of the procedure followed after the latex has issued from the trees, it is, clearly, necessary that the procedure should be maintained strictly uniform for different lots of latex and coagulum, particularly at those points, such as dilution of the latex, the milling and the drying, where variations from a uniform procedure are most likely to cause variation in the vulcanizing properties of the product.<sup>2</sup>

Estates differ a good deal in the care with which the factory work is organized, and the closeness and conscientiousness with which it is supervised. They differ a good deal in the extent to which the importance of strict uniformity, even in apparently minor details, is held in view. It would not be unfair to say that in the case of almost all estates some improvement, and in the case of many estates a very considerable degree of improvement, in regard to the uniformity of the rubber of any one grade produced is capable of being brought about by improved organization and supervision of the factory operations.<sup>3</sup>

<sup>1</sup> Observations on trees from four to eighteen years of age indicated that the increase of rubber-content was 1-2 per cent. per annum (Whitby, *Ann. Bot.*, 1919, **31**, 314).

<sup>2</sup> Cf. Eaton, *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 376.

<sup>3</sup> Bulking tanks are undoubtedly an important aid in securing uniformity of working conditions.

In the author's opinion the determination of the rubber-content, the dilution and the coagulation of the latex should always be done under immediate European supervision.

But, in view of the existence of physiological factors in variation, uniformity is not generally to be secured merely by standardizing the factory operations. Bulking the latex from different groups of trees naturally suggests itself as the most suitable method of neutralizing as far as possible the influence of the physiological factors capable of producing variation. The outlines of a complete system of receiving, bulking and coagulating tanks for dealing with a large volume of latex derived from different groups of trees have been given earlier (p. 142). No adequate data are available on which any conclusion may be based as to extent to which it is necessary to carry bulking in order to neutralize the influence of the physiological factors in variation. Probably the extent varies very considerably on different estates, and could be decided definitely for any one estate only by a systematic survey of the vulcanizing properties of the crop from the different areas into which the estate is divided for working purposes. In our present state of knowledge, the only safe recommendation appears to be that bulking should be on the largest scale feasible.

So far as the present writer knows, the largest bulking tank now in operation is one, built at his instance, with a capacity of 18,000 litres (4000 gallons). Volumes of latex containing more than one ton of rubber are regularly and successfully coagulated for crêpe preparation in this tank.<sup>1</sup> On most estates bulking, when practised, is conducted on a much smaller scale than that just mentioned—usually the volume of the bulking vessels is from one hundred up to several hundred gallons.

The preparation of a uniform product in the form of crêpe undoubtedly offers fewer difficulties than the preparation of such a product in the form of sheet.

*Examples of influence of bulking on variation.*—A few of a number of examples which have been put on record of the extent to which bulking and the adoption of a standard dilution has rendered the product less variable may be mentioned. (1)<sup>2</sup> During a period of rather more than two years, samples of rubber were taken at monthly intervals from an estate preparing crêpe in two factories from divisions of nearly the same age. In April

<sup>1</sup> In practice it is found advisable to build such a tank in duplicate, so that it is not necessary to remove all the coagulum from the tank in the morning in order to make ready for the reception of the day's latex. If coagulum is removed from the serum and then has to stand for several hours before being milled, it hardens considerably, and thus puts more work on the mills.

<sup>2</sup> De Vries and Spoon, *Archief*, 1919, 3, 246.

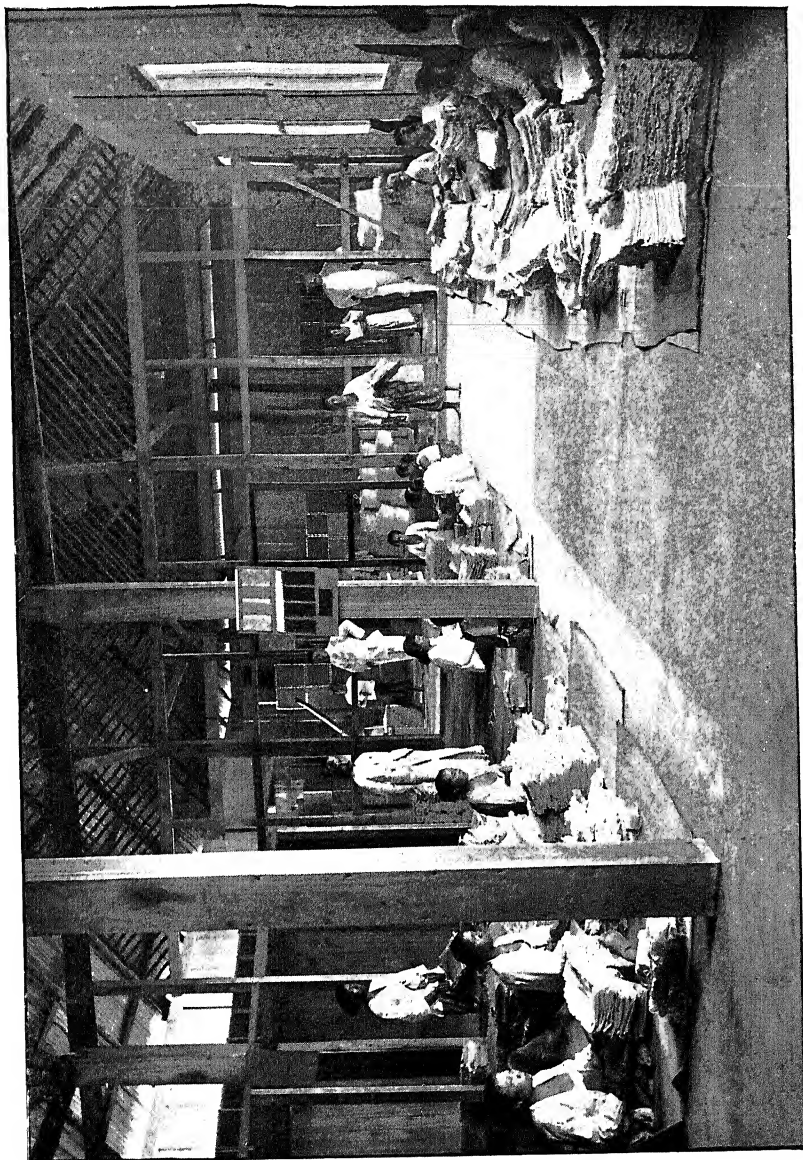


PLATE VI. Sorting and Packing Latex Crêpe.

1917 a standard dilution and bulking were adopted. The following table shows that their adoption reduced the degree of variation of the crop, as indicated by the figure for the average deviation from the mean, to about half its former value :—

TABLE LVII

	Division.	Time of cure.	
		Mean.	Limits.
Nov. 1916–Mar. 1917 (Procedure not standardized) }	T	116 ± 9	105–130
	Tj	107 ± 5	100–115
Apr. 1917–Dec. 1917 (Standardized procedure) }	T	130 ± 2½	125–135
	Tj	124 ± 3	120–130
Jan.–Dec. 1918 (Standardized procedure) }	T	127 ± 2	120–130
	Tj	122 ± 4 <sup>1</sup>	110–130

(2)<sup>2</sup> From a given estate fifty-three samples in all were taken. During 1916, when the estate was working in the old way, receiving the latex in 200-litre jars without bulking and without diluting to a standard rubber-content, the mean time of cure was  $113 \pm 5.6$  (limits: 105–130). In 1917 a standard dilution of 15 per cent. was adopted, but the latex was not bulked and not improbably the dilution was not carried out with exactitude. The average time of cure up to August 1917 was  $116 \pm 5.3$  (limits: 105–130). In August 1917 a standard dilution and bulking were adopted; and the average time of cure was  $118 \pm 2.3$  (limits: 110–120). For the first ten months of 1918 the time of cure was very uniform, the mean being  $120 \pm 0.5$  (limits: 120–120).

(3)<sup>3</sup> During 1915 an estate used a bulking tank, but did not dilute the latex to a fixed rubber-content. Eighteen samples were taken throughout the year, and their viscosity was determined. The viscosity (in relative figures) ranged from 81 to 164. Later, dilution to a fixed rubber-content was adopted; and in twenty-five samples taken over a period of one year the viscosity ranged only from 91 to 105.

In regard to the examples quoted above, the extent of the bulking is not stated.

In some cases, it would appear, the conditions on an estate may be so uniform that the product shows a fair degree of

<sup>1</sup> Excluding two months, when the samples cured particularly quickly, viz. in >115 and >110 minutes, the mean is  $123 \pm 3$ .

<sup>2</sup> De Vries and Spoon, *loc. cit.*

<sup>3</sup> Ultée, *Archief*, 1919, 3, 24.

uniformity in vulcanizing properties even without bulking. De Vries and Spoon<sup>1</sup> give data for a rather small estate (700 acres), the product from which was tested on forty-eight occasions over a period of two and a half years (1916-18). The latex was not bulked but was merely received in jars just in the order in which it arrived at the factory without regard to the part of the estate from which it had come. The results obtained were as follows:—

TABLE LVIII

Time of cure (mins.)	1916.		1917.		1918.	
	Mean	122 ± 2.5	125 ± 4	119 ± 2.5	110 ± 2.5	110 ± 2.5
	Limits	120 — 125	115 — 125	110 — 125	110 — 125	110 — 125

*Packing and variation.*—The packing of the crop has an importance in regard to uniformity, which has not yet been sufficiently realized to receive practical recognition, but which is such that it seems certain that the present random packing must be modified.<sup>2</sup> At present it is usual to pack the dry rubber from the drying sheds in a quite haphazard way, just as it comes to hand, or after a sorting on the basis of its tint; that is to say, it is usual to pay no account to the origin of the rubber or to probabilities regarding its uniformity. It would seem desirable, particularly where large bulking tanks are used, to pack all the rubber derived from one lot of latex together, and to indicate by suitable marks on the cases or on the shipping schedules exactly which groups of cases are likely to be uniform, as being (a) (smaller groups) derived from a single lot of latex; (b) (large groups) derived from the same area on different days.

With the object of neutralizing as far as possible variation in the plantation product, it is customary to blend different lots of rubber in making mixes for the manufacture of rubber goods. That the rate of cure of a blend of rubber samples of different individual rates of cure is likely to correspond, at least approximately, to the arithmetical mean of the individual rates of cure is indicated by some experiments published by Eaton<sup>3</sup> on the rate of cure of mixtures of matured crêpe with a time of cure of one hour, and thin crêpe with a time of cure of three hours. A mixture containing 33.3 per cent. of the slow crêpe cured in one and a half hours, one containing 50 per cent. in one and three-quarter hours, and one containing 66.6 per cent. in two and a quarter hours.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Cf. Whitby, "Some Notes on Standardization," *I.R.J.*, 1914, 48, 805.

<sup>3</sup> *Loc. cit.*, p. 321.



PART II  
THE TESTING OF RUBBER

## CHAPTER X

### THE STRESS-STRAIN RELATIONS OF RUBBER—THE MODULUS OF ELASTICITY

*Uniqueness of the stress-strain relations of rubber.*—The stress-strain relations presented by rubber are unique in their character. This uniqueness may be gathered from consideration of the following respects in which the behaviour of rubber is in strong contrast to that of almost all other materials:—

(1) Rubber is the only material in which the modulus of elasticity (Young's modulus), defined as the stress required to double the length of a piece of unit cross-section, is not an abstract quantity. Whereas metals stretched to their breaking-point may show an elongation of 30 per cent., rubber stretched to its breaking-point may show an elongation of more than 900 per cent.

(2) Rubber does not obey Hooke's law (constant proportionality between stress and strain within the elastic limits). The value of the modulus of elasticity within the elastic limits changes continually in a complex manner.

(3) Rubber does not show a "yield point" at which the material "draws out," but rather shows the converse condition, namely, what may be called a "firming-up point," beyond which it offers much greater resistance to extension than before.<sup>1</sup>

<sup>1</sup> *The elastic limit of rubber.*—It seems advisable to add a note on the definition of the elastic limit in the case of rubber. Some authors, apparently, would place the elastic limit of rubber at comparatively small deformations, such that, on removing the deforming force, the rubber shows practically no set and returns immediately to its original form. Shedd and Ingersol (*Phys. Rev.*, 1904, **19**, 114) would place the elastic limit not merely at the limiting deformation from which the rubber returns to its original state; they would further specify that, on removing the deforming force, the rubber must "repeat its previous history in exactly reversed order," *i. e.* it must not show a hysteresis loop.

But, in fact, there is probably no deformation, however small, which does not produce some (perhaps inappreciable) set, and recovery from which does not show some hysteresis. It appears that in the case of high-grade rubber what is sometimes called *permanent* set may be, strictly speaking,

The contrast between the stress-strain relations of rubber and those of, say, a metal wire may be seen by a glance at the following diagrammatic representation of the general course of the stress-strain curves for rubber and for a metal.

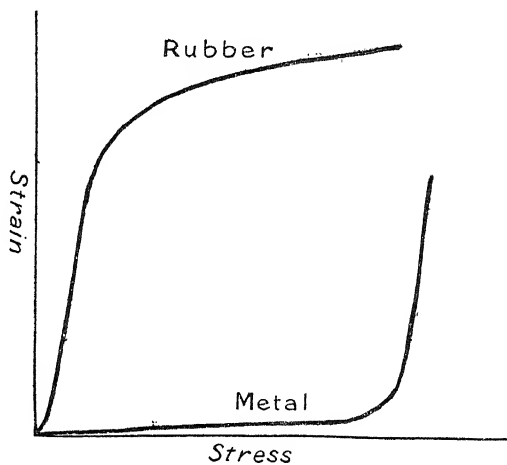


FIG. 4.

Speaking broadly: the metal is at first resistant to the pull and lengthens only slightly, until it reaches the "yield point," when it "draws out" with little or no increase in the stress,

wholly or in large part *sub-permanent* set: the set which is present after subjection to severe deformation disappears slowly. It may be considered that in regard to recovery from deformation rubber shows right up to its breaking-point a behaviour essentially similar to the behaviour of metals *within their elastic limits*; always bearing in mind that, owing to its vastly greater deformability, the absolute magnitude of the deviations from theoretically perfect elasticity are exaggerated: that, in a phrase of Bouasse's, the properties of rubber are "extraordinairement grossies et comme caricaturalles."

Even in the case of metals, the definition of the elastic limit does not contemplate theoretically perfect elasticity, but recognizes the existence of set and hysteresis within the elastic limits. Thus, for example, the definition of the elastic limit given by J. A. Ewing (*The Strength of Materials*, Cambridge, 1906, p. 10) is as follows: "The limits of stress within which strain is wholly or almost wholly elastic" (italics not in original). And again (p. 24): "Probably there is no stress, however small, that does not produce some permanent effect. There is always some slight hysteresis or lagging in the relation of strain and stress."

Hence, it is difficult to see how the elastic limit of rubber is to be placed at any point short of the breaking-point. This was already recognized by Stévant, who wrote in 1870: "le caoutchouc semble n'avoir d'autre limite d'élasticité que la rupture."

and then breaks; the rubber stretches easily at first, and then enters on a stage in which it offers greatly increased resistance to the pull and stretches very little as the pull is increased to the breaking-point.

#### THE RUBBER STRESS-STRAIN CURVE

The course of the relations between stress and strain on stretching rubber to the breaking-point was first investigated by Villari.<sup>1</sup> The most extensible of the samples investigated by him broke under a stress of 0.98 kg./mm.<sup>2</sup> and at an elongation of 559 per cent. Villari concluded that "rubber, different from all other known bodies, has three elastic coefficients": a first, or smallest, approximately constant; a third, or largest, also approximately constant; and a middle or variable one which increases quickly and connects the first and the third. If Villari's data for stress and strain throughout the stretching are plotted, they will be found to reveal the typical rubber stress-strain curve; but Villari's treatment of them is not entirely satisfactory.<sup>2</sup>

Stévant,<sup>3</sup> about the same time, also investigated the course of the stress-strain relations on stretching, but did not proceed to a sufficient extension to bring out the relations in their completeness. The rubber employed was of a pale red colour and a specific gravity of 1.06. The maximum elongation in any of the observations was 468 per cent. (corresponding load: 0.55 kg./mm.<sup>2</sup>). Mallock<sup>4</sup> exhibits the relations between stress and strain in a soft rubber carried to the breaking-point ( $L_{11}$ , 900 per cent.;  $P_{11}$ , 820 lb./in.<sup>2</sup>) by a curve which shows the general character of the stress-strain curve for high-grade rubber fairly satisfactorily.<sup>5</sup>

The following, selected more or less at random from the results of tensile tests made by the present author, shows the

<sup>1</sup> *Cimento*, 1869, 28 (2) I, 332, 361; *Ann. der Phys.*, 1871, 143, 88, 290.

<sup>2</sup> At all events in the German account of them. Bouasse has already remarked on the fact that some of the conclusions stated by Villari do not seem to be derivable from his data.

<sup>3</sup> *Résultats d'Expériences sur l'Elasticité du Caoutchouc vulcanisé*, Bruxelles, Paris, 1888. (Originally published: *Bull. du Musée de l'Industrie de Belgique*, 1870, 57, No. 5.)

<sup>4</sup> *Proc. Roy. Soc.*, 1889, 46, 233.

<sup>5</sup> The curve shown by Mallock bends over, before proceeding on the last stage, with excessive sharpness. This may have been due to the method of loading employed and to the intervals between readings.

typical form of the stress-strain curve for a rubber-sulphur vulcanizate of good tensile properties.

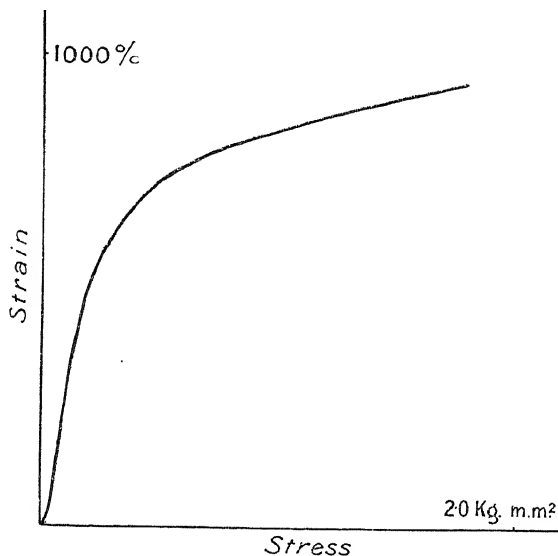


FIG. 5.—Stress-strain curve of a sample of vulcanized rubber. (Smoked sheet, cured for 2½ hours at 140° with 8 per cent of sulphur. Ring test-piece,  $4 \times 3.15$  mm., gave  $P_B : 1.73$ ,  $L_B : 1044$ , "Slope" : 35.)

Loads are referred to the original cross-section. It will be seen that, speaking broadly, the curve consists of three branches, namely: a first, very steep and almost straight portion, over which the material is very extensible; a third, comparatively flat portion, also almost straight, over which the material is tenacious; a second portion, in which the curvature changes rapidly, connecting the first and the third portions, and over which the extensibility of the material is changing continually. It will be seen that, included in the first portion, or, as may perhaps be said, introducing the first portion, is a short portion, over which the rubber is distinctly less extensible than it shortly becomes: there is a point of inflexion soon after the curve leaves the origin.

The curve shown above is typical of high-grade rubber compounds. The influence on the character of the curve of the addition to rubber of increasing quantities of inorganic materials is, speaking broadly, as follows: the first and last branches of the curve become less strongly contrasted in their inclination:

the curve approximates more and more to a straight line, or even begins to assume the character of the curve, represented above in a diagrammatic fashion, characteristic of a rigid material such as a metal. For most technical purposes rubber is mixed ("compounded") with inorganic materials. But it will be advisable to direct attention chiefly to the stress-strain curve for so-called pure gum compounds, *i. e.* the highly extensible vulcanized rubber prepared from raw rubber and sulphur only; because such compounds display the *characteristic* stress-strain relations of rubber more clearly than do other compounds, and because in most published researches, as distinguished from factory investigations, which are seldom made public, raw rubber has been tested in such compounds.

*Stress-strain curves for mineralized rubbers.*—Reference to Figs. 18 and 19, pp. 269, 271, which show the stress-strain curves for a number of samples examined by the Materialprüfungsamt and by the Bureau of Standards respectively, will serve to indicate the manner in which the course of the curve may be affected by the incorporation of inorganic materials ("compounding ingredients" or "fillers") with the rubber. The curves in these figures are drawn with stresses as ordinates and strains as abscissæ.<sup>1</sup>

The curve for Material I, in Fig. 18, shows what above has been called the characteristic rubber stress-strain curve. The greatest elongation given by this sample is in the neighbourhood of 850 per cent. No. 1 and No. 2, Fig. 19, show the curves for samples of a somewhat less extensible nature; the greatest elongation being less than 700 per cent. These two curves, while closely similar to the curve given by the highest-grade material, show a less marked contrast between the steep and the flat portions, and are shorter in their last stage. Material V, Fig. 18, in which the greatest elongation is about 500 per cent., shows a

<sup>1</sup> *En passant* the desirability of uniformity among rubber workers in the presentation of stress-strain curves may be mentioned. The curves are perhaps most easily handled if they run from left to right with strains as ordinates. The autographic attachment on the Schopper tensile testing machine traces the curves from right to left with strains as ordinates. Hence, it is perhaps hardly convenient for workers who employ this machine to present the curves running from left to right. The lack of a uniform practice as to the sense in which the curves run is, however, less inconvenient than the lack of uniform practice in representing strains as ordinates or as abscissæ.

The autographic attachment to the Schopper machine would be improved if it were made to trace the curves from left to right, and, especially, if the ratio of the stress scale to the strain scale were increased, in order to bring out the flat portion of the curve more clearly.

similar curve similarly truncated. Material IV, Fig. 18, which has a considerable tensile strength combined with a small elongation, and is probably rather highly mineralized, shows a curve very markedly different from the characteristic rubber stress-strain curve. And, in the low-grade Materials II, VI, VII, which have both low tensile strength and low elongation, the characters which mark the stress-strain curve for high-grade rubber are entirely absent.

#### THE ELASTIC MODULUS OF RUBBER

*Definition of the elastic modulus in the case of rubber.*—Hooke's law, which states that strain is proportional to stress, describes with considerable exactness the behaviour of metals subjected to stresses within their elastic limits, but, as a glance at the rubber stress-strain curve makes sufficiently obvious, does not hold for rubber. This circumstance, together with the fact of the great extensibility of rubber, make it necessary that circumspection shall be exercised in defining the modulus of elasticity in the case of rubber.

Ordinarily what is known variously as the modulus of elasticity, the coefficient of elasticity, Young's modulus, the stretch modulus<sup>1</sup> is regarded simply as the stress per unit cross-sectional area which would double the length of the material in question. And, thanks to the constant proportionality between stress and strain within the elastic limits, it is, in the case of metals, immaterial at what point in the stretching the modulus is determined, or over how long or how small a portion of the stretching it is determined. In the case of rubber, however, since the relation between stress and strain varies greatly at different points of the stretching, it is necessary to derive the value of the modulus at any point from only very small extensions—indeed, strictly, from an infinitely small extension,  $d\ell$ . If the modulus is to be regarded in the manner usual for other materials, as the stress per unit cross-sectional area which would double the length, there must be added to the definition the proviso: *on the assumption that the relation between stress and strain remains constant*. But since we know that in the stretching of a high-grade rubber over a long distance this assumption is not even approximately true, it seems advisable not to employ the ordinary definition of Young's modulus at all in reference to rubber.

<sup>1</sup> Of these terms only the last two are free from any ambiguity.

Further, since rubber extends so greatly that the cross-section of a sample at a given extension may be very much smaller than the cross-section in the unstrained condition, it is necessary to consider whether the stress at any point is to be referred to the actual cross-section or to the unstrained cross-section.

The elastic modulus may be referred to the original, unstrained length,  $L_0$ , and the original, unstrained cross-section,  $S_0$ , or it may be referred to the actual, strained length,  $L$ , and the actual, strained cross-section,  $S$ . If  $dL$  is the increment of length produced by an increment of stress  $dP$ , the modulus ( $E_1$ ) in the latter case is:—

$$E_1 = \frac{dP}{dL} \cdot \frac{L}{S}$$

and the modulus ( $E_2$ ) in the former case is:—

$$E_2 = \frac{dP}{dL} \cdot \frac{L_0}{S_0}.$$

Obviously the manner in which the elastic modulus is represented as changing during the course of stretching will differ according to the definition of  $E$  which is adopted. Villari,<sup>2</sup> who was the first to investigate the change of the elastic modulus of rubber during the course of stretching, calculated the modulus under the first form. The value of the cross-section,  $S$ , at each point was ascertained as follows: the diameter of the circular cord employed was determined at several points during the course of the stretching by means of a comparator; the volume corresponding to each measurement of the diameter was calculated; and, from the mean of the figures for the volume, the cross-section at any length,  $L$ , was calculated as  $S = V/L$ , on the assumption that the volume of the rubber remained con-

<sup>1</sup> Mention should be made of a third method of expressing the modulus. We may write—

$$E_3 = \frac{d\left(\frac{P}{S}\right)}{dL} L.$$

This expression is used by Cantone (*Rend. Ist. Lomb.*, 1898, 31) under the form—

$$E_3 = \frac{\frac{P'}{S'} - \frac{P}{S}}{\log L' - \log L}.$$

It cannot, however, be considered as a very useful method of expressing the modulus.

<sup>2</sup> *Cimento*, 1869, 28 (2) I, 332, 361; *Ann. der Phys.*, 1871, 143, 88, 290.



stant. This method of determining the volume by measurements of the diameter is a weak point in Villari's observations. The volume can be determined more readily and certainly by hydrostatic weighing.

The following shows a typical series of Villari's observations :—

TABLE LIX  
*Rubber cord, 117.84 mm. long, 3.75 mm. diameter*

Load (gms.) P.	Length (mm.) L.	Increment of length (dL) per 50 gms. (dP).	E <sub>1</sub> ' (kg./mm. <sup>2</sup> )
50	117.84		
100	123.96	6.12	0.08910
150	131.88	7.92	0.0763
200	141.60	9.72	0.0703
250	151.36	9.79	0.0807
300	162.84	11.48	0.0785
350	176.38	14.54	0.0716
400	191.00	15.22	0.0803
450	208.74	17.14	0.0842
500	227.14	18.40	0.093
550	247.00	19.86	0.1021
600	266.00	19.40	0.1121
650	286.36	19.96	0.1397
700	306.56	20.20	0.1595
750	325.28	18.72	0.1973
800	343.26	17.98	0.2313
850	360.92	17.66	0.2622
900	377.36	16.44	0.3113
950	393.48	16.12	0.3471
1000	409.00	15.52	0.3920
1100	436.84	13.92	0.4721
1200	468.50	15.83	0.4737
1300	490.28	10.89	0.7918
1400	515.92	12.82	0.7369
1500	536.80	10.44	1.0019
1600	559.70	11.45	0.9889
1700	577.90	9.10	1.3528
1800	597.80	9.60	1.3189
1900	616.10	9.15	1.5347
2000	636.46	10.18	1.4652
2200	662.30	6.46	2.4624
2400	684.80	5.62	3.0647
2600	703.60	4.70	3.9216
2800	719.52	3.98	4.8876
3000	742.00	5.62	3.6206
3200	Broke		

Stévant and Mallock both refer the modulus ( $E_2$ ) to the original length and cross-section, but neither treats the matter entirely satisfactorily. Putting

$$E = \frac{P}{(L - L_0)} \cdot \frac{L_0}{S_0},$$

and assuming that the volume remains unchanged ( $L_0 S_0 = LS$ ), Mallock writes:—

$$E = \frac{P}{(L - L_0)} \cdot \frac{L}{S_0}.$$

He calculates from this formula the modulus throughout the course of the stretching up to the breaking-point. The samples, which were taken up to the breaking-point, were of original cross-section  $(\frac{1}{8} \text{ in.})^2$ . For measurements at small extensions samples of *ca.*  $(\frac{1}{2} \text{ in.})^2$  cross-section were used. It may be of interest to record the figures obtained in the case of different rubbers on samples of the above dimensions:—

1. A soft, grey rubber, sulphur-content }  $L_B \times P_B = 990 \times 820 \text{ lb./in.}^2$   
*ca.* 5.7 per cent., sp. gr. 1.289.
2. A red rubber, sulphur-content *ca.* 2.1 }  $L_B \times P_B = 730 \times 820 \text{ lb./in.}^2$   
per cent., sp. gr. 1.407.
3. A hard, grey rubber, sulphur-content }  $L_B \times P_B = 440 \times 820 \text{ lb./in.}^2$   
*ca.* 3.8 per cent., sp. gr. 2.346.

TABLE LX

1.		2.		3.	
$L_0 = 10 \text{ in.}$	$S_0 = 0.2690 \text{ in.}^2$	$L_0 = 10 \text{ in.}$	$S_0 = 0.2307 \text{ in.}^2$	$L_0 = 10 \text{ in.}$	$S_0 = 0.2625 \text{ in.}^2$
$L - L_0$	E.	$L - L_0$	E.	$L - L_0$	E.
0.228	124.9	0.163	161.1	0.038	497.0
0.385	125.3	0.345	163.0	0.078	491.2
0.530	129.2	0.471	166.9	0.115	502.2
1.77	123.9	1.430	166.5	0.156	495.7
4.85	114.0	3.390	164.5	0.360	463.5

In constructing the rubber stress-strain curve, it is now the invariable custom to refer the stress to the original cross-section. Hence, in a first view, the inclination of the curve at any point gives  $E_2$  directly at that point. The inclination of the curve,  $\frac{dP}{dL}$ , differs from  $E_2$  only by the factor  $L_0/S_0$ .  $E_1$  is not given directly by the stress-strain curve. But it may readily be derived from  $\frac{dP}{dL}$  by multiplying the latter by the square of the actual length at any point,  $L^2$ . For, assuming that the volume

### THE DEFINITION OF $\epsilon$ AND $\epsilon'$

of the rubber does not change— $\epsilon' = \frac{\Delta l}{l_0} = \frac{\Delta l}{l_0} = \frac{\Delta l}{l_0}$ —we have

$$\epsilon' = \frac{\Delta l}{l_0} = \frac{\Delta l}{l_0} = \frac{\Delta l}{l_0}$$

that is to say, it suffices to divide the  $\frac{\Delta l}{l_0}$  obtained by the actual length to obtain  $\epsilon'$  in relative terms.

### THE WORK OF ROMANSCOFF

The most satisfactory treatment which we have of the modulus of elasticity of rubber is contained in a paper<sup>1</sup> due to him by Romanseff,<sup>2</sup> who approached the question after the manner<sup>3</sup> in the investigation of the elastic properties of various materials, metallic wires, etc. Romanseff sets himself to determine  $\frac{\Delta l}{l_0}$  by actual measurement, for rubber under different conditions, by describing small cycles of extension and retraction. Two chief methods were adopted for the measurement of  $\frac{\Delta l}{l_0}$ , namely, a dynamical one, in which the rubber was maintained at constant length, and a statical one, in which the rubber was kept under constant load.

The whole of the observations of Romanseff, and also of Romanseff and Carrère (described later), were made on portions of the same sample of rubber, viz. a cord, 4 mm. in diameter, consisting of gum and sulphur only and having a specific gravity of 0.986. It is recognized that similar exhaustive observations should be made on other varieties of rubber. And it may be said, if it is particularly desirable in regard to the influence on the modulus of previous operations, of periods of rest and of temperature changes, that similar exhaustive observations should be made on other varieties of rubber. A comparison of different compounds and of different states of cure in the same compound, while presenting an extensive programmatic for investigation, would probably be very illuminating.

Throughout Romanseff's work  $\frac{\Delta l}{l_0}$  is represented by  $\epsilon$ , and the

<sup>1</sup> *Annales de la Faculté des Sciences de Toulouse*, 1904, 8, 5-11.

<sup>2</sup> *Id.* *Ann. de Chim. Phys.*, 1905, 29, 1-104.

<sup>3</sup> Or, more strictly speaking,  $\frac{\Delta l}{l_0}$ .

sign  $\Lambda$  is used to represent the length of the rubber when the original length is taken as 1.

# DYNAMICAL MEASURE OF $\frac{dP}{dL}$ .

This method depends on observing the alteration in the period of oscillation of a pendulum which is brought about by attaching to the pendulum the strip of rubber the elastic modulus of which it is desired to investigate.

Let a pendulum be suspended at O. Let M be its moment of inertia,  $C\theta$  the couple due to the weight for an amplitude  $\theta$ . Then the period of oscillation,  $T_1$ , is given by :—

$$T_1 = 2\pi \sqrt{\frac{M}{C}}.$$

If, now, the middle of a strip of rubber AC, which can be stretched more or less between A and C, is fixed to the pendulum at B, then when the pendulum oscillates, the point B will be displaced by a length  $d$ , and,  $dP/dL$  being represented by  $\epsilon$ , the couple which results from the variation of tension of the two halves of the rubber acting in the same sense will be  $2\epsilon d^2\theta$ . And under the combined influence of this couple and of the weight the period of oscillation will become :—

$$T_2 = 2\pi \sqrt{\frac{M}{C + 2\epsilon d^2}}.$$

From these expressions we get :—

$$\epsilon = \frac{C}{2d^2} \cdot \frac{T_1^2 - T_2^2}{T_2^2}.$$

Absolute measures of  $\epsilon$  can be made, but it is more convenient to state  $\epsilon$  in relative terms. As the factor  $C/2d^2$  was constant, relative values for  $\epsilon$  could be obtained simply from the values

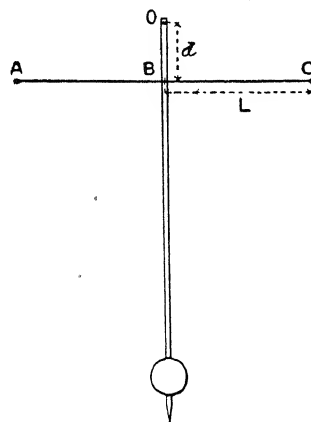


FIG. 6.

( $T_1$  and  $T_2$ ) for the period of oscillation without and with the rubber attached.

It is necessary to be able to maintain the oscillations at constant amplitude during the measurement of the period of oscillation or for any period. The experimental problem which this necessity presents is somewhat difficult. Mallock,<sup>1</sup> who had earlier measured the elastic modulus of rubber by a similar dynamical method, made no provision for maintaining the amplitude of the vibrations, but determined the duration of oscillations of rapidly decreasing amplitude.

The essentials of Bouasse's experimental arrangement are shown diagrammatically in Fig. 7.

The pendulum oscillates round the horizontal axis O. It carries the masses PP', the light, horizontal, wooden rod EF, and a curved magnet RS, of which the centre is at the point O. The copper points, *a* on the one side and *b* and *c* on the other, make contact with cups of mercury when the pendulum has moved a little to the right or to the left respectively of the vertical. At *h* is another contact. This is made at the instant that the pendulum passes through the vertical position. By means of an auxiliary arrangement, not shown in the figure, the coils *e* and *f* are made to act only alternately as the pendulum passes over to either side of the vertical position. By adjusting the strength of the current by means of a rheostat, the amplitude of the oscillations of the pendulum can be maintained constant over a period of hours or even of days. The period of oscillation was determined to within a hundredth of a second by Hipp's chronoscope, actuated through a contact at *b*, or by taking the time of 50-100 oscillations with a stop-watch.

AC is the rubber cord attached at its mid-point to the pendulum at B. For the purpose of making observations with the rubber at temperatures other than the room temperature, each half of AC is surrounded by a jacket through which hot water can be circulated. Only one of these jackets is shown in the figure. There is a further auxiliary arrangement, not shown in the figure, for stretching the rubber cord equally over both halves, so that the point B remains the mid-point of the rubber and the tension of the two halves remains equal. The movement of the point B is about one-seventh of that of the tip of the pendulum, *h*. In general the movement of the latter was

<sup>1</sup> *Loc. cit.*

10 cm. Hence, the amplitude of the sinusoidal elongation of the rubber—half its total elongation—was about 0.72 cm.

*Variation of modulus during cycles of extension and retraction.*—The following data show the manner in which  $\epsilon$  was found to vary at different points between lengths  $\Lambda = 1$  and  $\Lambda = 5$ , and

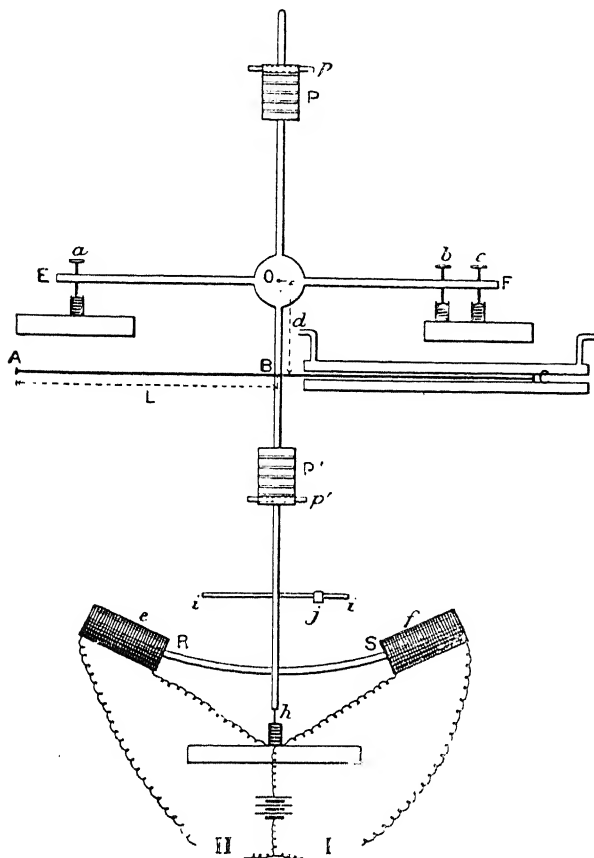


FIG. 7.

also show the effect on  $\epsilon$  of repeating the cycle of extension and retraction:

$L_0$  was 18 cm. The value of  $\epsilon$  was determined at the six points indicated. At each point three minutes were allowed to elapse before  $\epsilon$  was measured; observations were then made over twenty oscillations. The cycle between  $\Lambda = 1$  and  $\Lambda = 5$

was repeated three times. The following table shows the values obtained in the first and third cycles:—

TABLE LXI

	L (cm.)	. . .	25	35	50	65	80	90
Cycle I. $\epsilon$	{ Extension	. . .	473	296	281	351	566	816
	{ Retraction	. . .	413	243	192	214	340	
Cycle III. $\epsilon$	{ Extension	. . .	413	225	184	194	290	460
	{ Retraction	. . .	418	230	179	193	267	

The rubber was now left for a few hours, and, in the afternoon, five cycles,  $\Lambda = 1$ ,  $\Lambda = 5$ , were described without any stops, and then a cycle (Cycle IX) with halts for the determination of  $\epsilon$  was described, with the following results:—

	L.	. . .	25	35	50	65	80	90
Cycle IX. $\epsilon$	{ Extension	. . .	392	221	178	186	255	398
	{ Retraction	. . .	407	222	170	180	243	

The general conclusions which the observations indicated are as follows:—

(1) The modulus  $E_x$ , determined at constant length, decreases as the extension increases; passes through a minimum, remaining comparatively constant, however, over a considerable range of lengths (say, between  $\Lambda = 2$  and  $\Lambda = 4$ ); then increases very quickly up to the greatest extensions possible.

It is a little unfortunate that Bouasse's observations do not cover more completely the later portions of the stretching to which the rubber was capable of being subjected.<sup>1</sup> There is, however, little doubt that the modulus continues to increase over the whole of the "flat" portion of the stress-strain curve.

(2) As the number of cycles increases, the values of the modulus for a given extension diminishes, at first quickly, then slowly. After a number of cycles the values tend to become fixed. The values of  $\epsilon$  at  $\Lambda = 5$  in the first three cycles were

<sup>1</sup> Presumably the greatest length at which observations were taken was limited to  $\Lambda = 5$  or  $\Lambda = 6$  because of the difficulty of gripping the rubber at greater extensions. The problem of gripping the specimen satisfactorily at high extensions is one of the most important of the problems of technique in connection with the exhaustive investigation of the stress-strain relations of rubber (cf. Chap. XI).

And, further: the shape of the specimens used by Bouasse was not suited to showing the highest extensions of which the rubber in question was capable. The more recent investigations into the influence of the shape of the specimen on the point of failure made by Memmler and Schob (cf. Chap. XI) revealed the fact that specimens with parallel sides are unsuitable for showing the maximum extension of which a rubber is capable.

816, 535, 460. The cord was a fresh one, and was stretched for the first time in Cycle I. The first cycle shows results very markedly different from those shown by any subsequent cycle. The distinctiveness of the first cycle may also be seen in observations of Bouasse and Carrière, of Schwartz and of others, on tracing hysteresis loops, which are described in Chap. XVIII.

(3) The moduli show very great hysteresis in the first cycle. The hysteresis diminishes as the number of cycles increases; in the third cycle it is already small, and in Cycle IX is almost absent. The relation between  $\epsilon$  and  $\Lambda$  for Cycle I and for Cycle IX is shown in the following figure:—

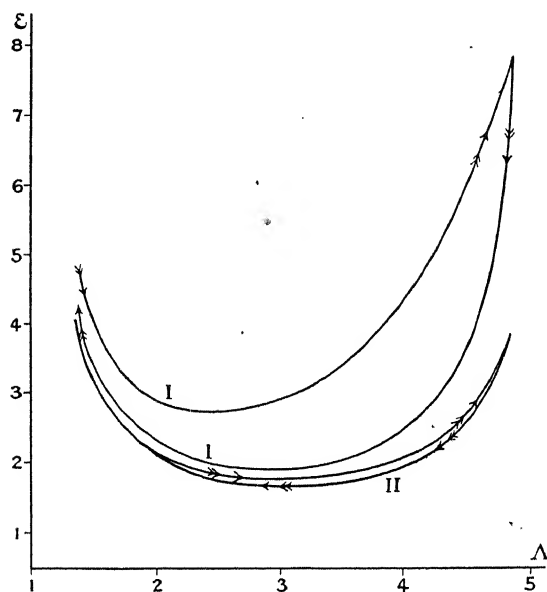


FIG. 8.

Bouasse remarks that the above three general conclusions hold for all types of rubber, even those containing a high percentage of fillers.

*Variation in  $E_1$ .*—As already mentioned,  $\epsilon$  is directly proportional to  $E_2$ , but, in order to get  $E_1$  (in relative terms), the values of  $\epsilon$  must be multiplied by  $L^2$ . Calculating  $E_1$  for the first cycle, we get:—



TABLE LXII

	L.	.	.	25	35	50	65	80	90
	$\Lambda$	.	.	1.38	1.94	2.77	3.66	4.44	5.00
Cycle I. $E_1$ (in arbitrary units)	{	Extension	.	100	123	240	507	1237	2270
		Retraction	.	87	101	164	309	743	

It is seen that  $E_1$  increases continually with increase of extension. At first the increase is comparatively slow, then very rapid;  $E_1$  at a length of 500 per cent. being 22.7 times as large as at a length of 138 per cent. The other cycles show similar results. This conclusion is in accord with the conclusion as to the change of  $E_1$  with increasing extension which was indicated by the results of Villari. One series of Villari's observations has been quoted. In this particular series, it may be stated for purposes of comparison, the change of  $E_1$  over the range of length just mentioned is approximately 1 to 18. Villari's measurements, it may be mentioned, extend to a somewhat greater extension than  $\Lambda = 5$ , and show that the increase of  $E_1$  continues beyond  $\Lambda = 5$ .

*The modulus at small extensions.*—For the investigation of the modulus at small extensions, below the first one in the cycles referred to above, Bouasse took a new portion of cord, and found the following results:—

TABLE LXIII

*Cycle between  $\Lambda = 1$  and  $\Lambda = 1.330$*

	$\Lambda$	.	.	1.055	1.110	1.165	1.220	1.275	1.330
$\epsilon$	{	Extension	.	889	800	720	660	593	555
		Retraction	.	855	766	684	626	578	
$\epsilon \Lambda^2$ (i. e. $E_1$ in arbitrary units)	{	Extension	.	989	968	977	982	964	982
		Retraction	.	952	927	928	931	960	

It will be seen from these figures that:—

(1) At small extensions  $\epsilon$  falls with increasing extension, thus coming in line with the earlier measurements.

(2)  $E_1$  appears to be approximately constant at small extensions. The mean value of  $E_1$  during the extension is, in the case quoted, 977. The deviations from this value are of the order of the experimental error. The observations of Villari and of Mallock may also be regarded as in accord with the conclusion as to the practical constancy of  $E_1$  at small extensions.

STATIC METHOD OF MEASURING  $\frac{dP}{dL}$

The apparatus employed is represented diagrammatically in the following figure :—

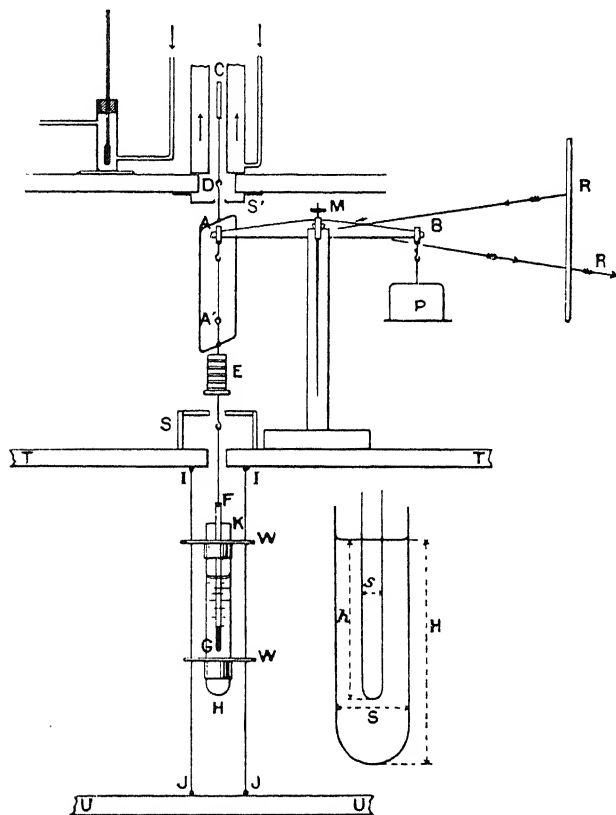


FIG. 9.

The essential part is the beam, AB, of a sensitive balance. The mirror, M, allows of the vertical displacements of the knife-edge, A, being measured with the aid of a telescope (not shown) and the divided scale, R. The rubber under investigation, C, is held in a clamp (not shown), which supports the rigid system, DE. The weights used for loading the rubber specimen and shown at E consist of split discs of lead, each

weighing 66 g. The cylinder, FG, which is loaded with mercury, dips into a tube, KH, containing water. The mountings, W, pass round the guides, IJ, which consist of taut metallic wires firmly fixed in position. With the aid of an eccentric, a sinusoidal movement is given to the system formed by the cylinder, KH, and its mountings. The eccentric (not shown) is carried by a wheel to which a convenient uniform movement can be given. In this way the rubber, while under a definite mean load, can be subjected to slight variations of load, alternatively positive and negative, in a perfectly definite and regulable manner.

For the purpose of making observations at elevated temperatures, the rubber is surrounded by a jacket, which is indicated in the diagram. The extension of the rubber specimen is done from above by means of an auxiliary arrangement (not shown), and can be read by means of a second telescope. The purpose of the supports, S and S', is to prevent accidents in case of unexpected rupture of the specimen. The distance, AM, is 14 cm., and the distance of the mirror from the scale, R, 1 m. Hence, since  $\frac{1}{10}$  mm. could easily be read on the scale, variations in the length of the rubber were read to  $\frac{1}{140}$  mm.  $dL$  is measured, as indicated, on the scale, R.  $dP$  can be obtained from a knowledge of the dimensions of the plunger, FG, and of the cylinder, HK, and of the oscillatory movement to which the latter is subjected.<sup>1</sup>

<sup>1</sup> Let  $x$  be the variable length which fixes the position of HK;  $dx$  being reckoned positive when the vessels descend.  $L$ , the length of the rubber, determines the position of the plunger, FG.

Let  $h$  = the amount to which the latter dips into the water.

$H$  = the height of the water in HK.

$S$  = the internal cross-section of HK.

$s$  = the external cross-section of FG.

(See side diagram in Fig. 9.)

The volume of water is  $HS - hs$ , from which:—

$$(1) \quad SdH = sdh.$$

If HK is lowered,  $dx$ , the absolute level of the water, falls by  $dx - dH$ . But the rubber finds itself under a slightly increased load and lengthens by  $dL$ . Thus, the amount  $h$ , to which the plunger dips in the water, changes by

$$(2) \quad dh = -dx + dH + dL.$$

Now, if  $\delta$  = the specific gravity of the liquid,

$$(3) \quad dP = -sdh\delta; \quad dL = -\frac{s\delta}{\epsilon} \cdot dh.$$

From these equations, we have

$$dL = \frac{dx}{1 + \frac{s}{\delta s} \left(1 - \frac{s}{S}\right)}.$$

The statical method, in which  $\epsilon$  is determined at constant load, does not lend itself so easily to obtaining consistent values of  $\epsilon$  as does the dynamical method, in which  $\epsilon$  is determined at constant length.  $\epsilon$  varies with time somewhat in both methods, but much less when the length is fixed than when the load is fixed. It is necessary, therefore, in making measurements at constant load, to define the conditions, particularly as regards the time intervals, very precisely.<sup>1</sup>

*Change of modulus, as determined by the statical method, throughout cycles.*—The following example shows results obtained for  $\epsilon$  when the loads were increased in arithmetical progression, and 15 minutes were allowed to elapse under each load before  $\epsilon$  was determined. The increments of load were  $2\gamma$  ( $\gamma$  = the weight of one disc, *i. e.* 66 g.).

TABLE LXIV  
(L in hundredths of a cm.)

Load	0	2	4	6	8	10	12	14	16
Extension	{ L. 1622 $\epsilon$ 3932	2074 1585	2785 966	3889 732	5106 727	6239 845	7343 1208	8405 2342	9118 4100
Retraction	{ L. 1680 $\epsilon$ 2660	2227 1427	3056 886	4810 765	7275 1149	8291 1876	8738 2770	8940 3570	

The cord used in the above experiment was not a fresh one, but one which had been subjected on previous occasions to numerous cycles between the same limits. The manner in which the value of  $\epsilon$  is found to change in reference to change of length is essentially the same as that found by the dynamical method; the extension and retraction curves connecting  $\epsilon$  and L being similar to those shown in Fig. 8 for (Cycle IX) a sample which

Thus, for a given liquid and given dimensions of the plunger and cylinder, we have

$$= K \left( \frac{dx}{dL} - 1 \right).$$

In the apparatus employed the diameter of the plunger, FG, was never more than 11 mm. and that of the tube HK 35 mm. Thus, the ratio of  $s : S$  was 1 : 10. With the dimensions employed  $dx/dL$  was ordinarily about 40.

<sup>1</sup> As an example of the extent to which the elongation and the value of  $\epsilon$  under a given load may be altered by repetition of a given load-cycle, the following case mentioned by Bouasse may be noted. A cord 16 cm. in length is taken, and is subjected to cycles between 0 g. and 1060 g. As the number of cycles is increased, the length measured under 800 g. may increase from 65 cm. ( $\Delta = 4$ ) to 96 cm. ( $\Delta = 6$ ), and the value of  $\epsilon$  measured under the same load may change in the ratio 1 : 4.

had already been stretched a number of times. The curve representing  $\epsilon$  as a function of the load, however, shows a considerable hysteresis and has a somewhat singular character. It is shown in the following figure.

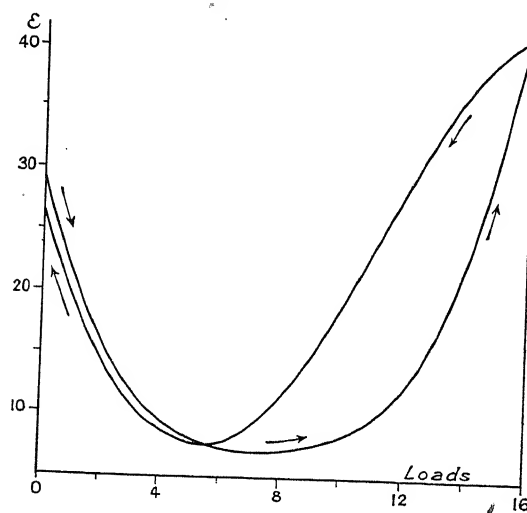


FIG. 10.

*The modulus not a definite function of  $P$  and  $L$ .*—Bouasse concludes from his work that, in general,  $\epsilon$  cannot be derived satisfactorily from the stress-strain curves, because the form of the latter is influenced greatly by elastic after-effect (cf. Chap. XIX).

The whole tendency of the work of Bouasse is to demonstrate the fact that  $\epsilon$  is not a definite function of  $P$  and  $L$ , but is influenced by the whole of the anterior operations to which the rubber has been subject. The results already quoted have provided examples of the extent to which the values for the modulus obtained in a given cycle are influenced by preceding cycles. The following results may be quoted as illustrating the influence on the values for the modulus of the range of the cycle and of periods of rest at different extensions.

*Influence of range of cycle and of periods of rest.*—The results shown below were obtained on four specimens, each previously unstretched, in the following way. The specimen was taken to the extreme point of the cycle, viz.  $\Lambda = 5, 3, 1.7, 5$ , and  $\epsilon$  was determined; the specimen was then brought to the initial point

of the cycle, viz.  $\Lambda = 1, 1, 1, 3$ ; it was returned at once to the extreme point, and, after a period of waiting,  $\epsilon$  was determined. Following this procedure,  $\epsilon$  was determined every 15 minutes. After a number of cycles, the specimen was allowed to rest for 105 minutes at the initial point of the cycle, and, after it had been taken again to the extreme point,  $\epsilon$  was again determined.

TABLE LXV

$\epsilon$  at the extreme point in successive cycles

Cycle $\Lambda = 1$ to $\Lambda = 5$	670	448	399	375	357 <sup>1</sup>	326	Rest 369	331
„ $\Lambda = 1$ to $\Lambda = 3$	221	188	180	174	171		„ 175	
„ $\Lambda = 1$ to $\Lambda = 1.7$	275	261	260	261			„ 259	
„ $\Lambda = 3$ to $\Lambda = 5$	620	614	592	385	571		„ 598	

It will be observed that, the shorter the cycle, the less marked is the diminution in  $\epsilon$  at successive cycles, and the smaller is the amount of recovery during rest.

Further, it is found that for a given extreme elongation, the amount of recovery is greater, the smaller the initial elongation.

Bouasse formulates the following rule: "Every stretching, every reduction in length, in general, every change of form tends to diminish the value of  $\epsilon$  corresponding to a given elongation. Every rest tends to augment  $\epsilon$ , and the augmentation increases in proportion as the position of rest is nearer  $\Lambda = 1$ ."

When considering, in relation to the latter part of this rule, figures such as those quoted above, it is to be borne in mind that the magnitude of  $\epsilon$  determined, after a period of rest, at the extreme point of a cycle is influenced, not only by the length of the period of rest and its remoteness from or proximity to  $\Lambda = 1$ , but also by the length of the cycle. Considering, for example, a cycle of which the extreme point is  $\Lambda = 5$ : on the one hand, the nearer the position of repose lies to  $\Lambda = 1$ , the greater will be the effect of rest in increasing  $\epsilon$  at  $\Lambda = 5$ ; but, on the other hand, the nearer the position of repose is to  $\Lambda = 1$ , the greater will be the effect in reducing  $\epsilon$  of the deformation involved in bringing the rubber from the position of rest to  $\Lambda = 5$ . Thus, in regard to the effect on  $\epsilon$  at a given extension of rest at an inferior extension, two opposed effects are to be considered; and it may be anticipated that, where  $\epsilon$  at a given extension has fallen considerably, there should be a certain inferior extension at which, in a given period of rest, the increase of  $\epsilon$  measured at the superior extension should be maximal.

<sup>1</sup> In this case a period of 105 minutes' rest under  $\Lambda = 5$  and three cycles intervened here.

*Optimum position of repose.*—The existence of such an optimum position of rest can be demonstrated. The following results may be quoted in this connection:—

A rubber cord,  $L_0 = 17$  cm., was subjected to four cycles between  $\Lambda_0 = 1.35$  and  $\Lambda_1 = 5.3$ , in order to reduce  $\epsilon$ . It was then brought to  $\Lambda_2 = 3.5$ , and  $\epsilon$  was measured. It was then brought again to  $\Lambda_1$ , and  $\epsilon$  was again measured. Measurements of  $\epsilon$  at  $\Lambda_2$  and  $\Lambda_1$  were made at intervals of 15 minutes.

*Cycles between  $\Lambda_2 = 3.5$  and  $\Lambda_1 = 5.3$*

$\epsilon$ at $\Lambda_2$	.	.	.	240	258	266
$\epsilon$ at $\Lambda_1$	.	.	.	710	888	

It will be seen that the effect of the period of rest at  $\Lambda = 3.5$  is to bring about an increase in  $\epsilon$  at  $\Lambda = 5.3$ , despite the opposed effect of the deformation from the former to the latter extension. In the case of the cycle  $\Lambda = 1$  to  $\Lambda = 5$ , it was noticed (Table LXV) that  $\epsilon$  showed a decrease after a period of repose at the inferior position.

The above specimen was now left in repose for 95 minutes at  $\Lambda_2$ . It then gave the following figures:—

$\epsilon$ at $\Lambda_2$	.	.	.	274	274	962
$\epsilon$ at $\Lambda_1$	.	.	.	970		

Four cycles,  $\Lambda_1\Lambda_0$ , were now described. After these,  $\epsilon$  at  $\Lambda_1$  had fallen to 593. After four hours' repose at  $\Lambda_1$ , it had risen to 702, and after 13 hours longer, to 754. The rubber was now brought to  $\Lambda_2$ , and measurements were made, as before, every 15 minutes.

$\epsilon$ at $\Lambda_1$	.	.	.	754	785	812
$\epsilon$ at $\Lambda_2$	.	.	.	269	274	

It will be observed that, while  $\epsilon$  rose only from 702 to 754 in 13 hours' repose at  $\Lambda_1$ , it rose from 754 to 812 in about 30 minutes' repose at  $\Lambda_2$ . The rubber was left in repose at  $\Lambda_2$ . After 25 hours,  $\epsilon$  at  $\Lambda_1$  had risen to 1000. For  $\epsilon$  at  $\Lambda_1 = 5.3$ ,  $\Lambda_2 = 3.5$  proved to be approximately the optimum position of repose. Observations made with a period of repose at  $\Lambda = 4.4$  and at  $\Lambda = 2.6$  showed a markedly smaller effect at either of these positions.

*An apparently anomalous case.*—Finally, there may be mentioned a somewhat striking case, in which the influence of repose is seen as having the apparently anomalous result of increasing the values of  $\epsilon$  in a subsequent cycle as compared with those

in a preceding one. The case is, however, in accord with the general rule which has been laid down.

A new specimen was subjected to several cycles between  $\Lambda = 1$ ,  $\Lambda = 6$ ; it was then left in repose at  $\Lambda = 2$  for 24 hours, and was then put through the cycle  $\Lambda = 4$ ,  $\Lambda = 6$  with halts, of 10 minutes, at  $\Lambda = 4$ , 4.66, 5.33, 6.

TABLE LXVI

$\Lambda$	.	.	.	.	.	4	4.66	5.33	6
Extension	.	.	.	.	.	132	175	267	551
Retraction	.	.	.	.	.	144	168	236	551
Extension	.	.	.	.	.	183	311	682	
Retraction	.	.	.	.	.	149	172	251	

The influence of temperature on the value of the modulus will be discussed later (Chap. XX).

*Influence of rate of extension and retraction.*—The influence on the values of  $\epsilon$  of the rate at which the small cycles in the statical method were described, *i. e.* the influence of the rate at which the variation of load,  $dP$ , was effected, was examined. It was found that the values of  $\epsilon$  observed were somewhat greater with a more rapid change of load than with a slower change, but to a smaller extent at the higher loads than at the lower ones. This result is what would be expected from our knowledge of elastic after-effect in rubber (cf. Chap. XIX).

In making the comparisons given below, the speed of the eccentric was changed in the ratio 1 : 3; the periods being 43 s. and 129 s. The table shows  $\epsilon$  with the slower period, the ratio of  $\epsilon$  with the faster period to  $\epsilon$  with the slower, and the time,  $T$ , for which the cord remained under the load in question before measurements were made.

TABLE LXVII

INFLUENCE OF THE SPEED WITH WHICH  $dP$  IS VARIED

Load ( $\gamma$ )	.	.	.	.	0	4	8	16
<i>Loading</i>								
$\epsilon$	.	.	.	.	1366	—	351	2688
Ratio of $\epsilon$ 's	.	.	.	.	1.044	—	1.019	1.019
$T$	.	.	.	.	12 hrs.	—	70 m.	280 m.
<i>Unloading</i>								
$\epsilon$	.	.	.	.	1248	434	789	—
Ratio of $\epsilon$ 's	.	.	.	.	1.045	1.043	1.023	—
$T$	.	.	.	.	30 m.	60 m.	16 hrs.	—

R



## FURTHER METHODS FOR DETERMINATION OF THE MODULUS

The determination of  $\epsilon$  by measurement of the rate of propagation of a disturbance in a rubber specimen will be discussed, in connection with the Joule Effect, in Chap. XX. It is there concluded that, although unsatisfactory in the form used by Stefan and by Exner, the method would, with a suitable technique, not improbably be capable of giving determinations of the elastic modulus of rubber which would be valuable for the investigation of certain questions.

Bouasse<sup>1</sup> has suggested an elegant method for the determination of the modulus, which, however, he concludes, does not give exact values. The method is essentially an adaptation of the well-known Melde's experiment. The rubber, held at one end by a clamp which can be moved along a fixed scale on which extensions can be read, is attached at its other end to an electrically maintained tuning-fork. In this way stationary longitudinal waves are produced in the rubber. Measurement of the position of the nodes, together with a knowledge of the period of the tuning-fork, enables the value of  $E_1$  to be determined.<sup>2</sup> The results are not, however, in general, very exact, owing chiefly to the difficulty of correcting for the effect of the damping of the vibrations.

*Variation of the modulus during cycles.*—The results obtained by Bouasse by this method, regarding the manner in which the modulus of elasticity varies during cycles of extension and retraction, are, however, similar in their general character to those obtained by the two methods, already described, of which he makes greater use. The following shows the results obtained with rubber cord ( $L_0 = 80$  cm.), which had been previously subjected to the several cycles mentioned below, at a number of points on the retraction curve from  $\Lambda = 5$ . The figures in the lower line give the length of the inter-node in cms. Since the tuning-fork made 50 vibrations per second, these figures

<sup>1</sup> *Loc. cit.*

<sup>2</sup> The length of the waves and the period of the tuning-fork enable the velocity of longitudinal propagation of the wave ( $v$ ) to be obtained from the relation  $\lambda = vT$ . And  $v^2$  is proportional to  $E_1$ .  $E_1$  is defined as  $\frac{dP}{dL} \cdot \frac{L}{S}$ . Newton's formula gives  $v = \sqrt{\frac{gE_1}{\delta}}$ ; the specific gravity of the rubber is regarded as constant. Hence,  $E_1$  is proportional to the square of the interval between the nodes.

also represent the velocity of propagation ( $v$ ) in the rubber in metres per second.

$\Lambda$	5.00	4.75	4.50	4.25	4.00	3.75	3.50	3.25	3.00
Inter-node and $v$	167	138	119	104	92	81	72	64	58
$\Lambda$	2.75	2.50	2.25	2.00	1.75	1.50	1.25		
Inter-node and $v$	52	48	44	41	40	40	40		

The figures in the lower line when squared give  $E_1$  in relative terms; and the values for the latter, when divided by  $\Lambda^2$ , give relative values for  $\epsilon$  and  $E_2$ . Representing graphically the change of  $v$ ,  $E_1$  and  $\epsilon$  with change of length of the rubber, we have the following curves, which have the same general character as corresponding curves derived from determinations of the elastic modulus by the other two methods.

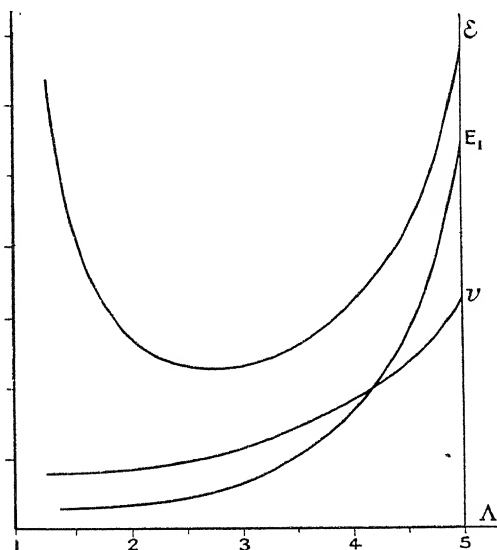


FIG. II.

It will be observed that  $E_1$  increases continually as the extension is increased, or, rather, in the case of the present experiment, falls continually as the extension decreases; that the velocity of propagation in the rubber also increases continually as the extension increases, but at a slower rate than  $E_1$ ; and that  $E_2$  first falls to a minimum, and then rises continually as the extension increases.

*Influence of a succession of cycles and of periods of rest.—A*

limited investigation of the influence of a succession of cycles and of periods of rest on the magnitude of the modulus at a given extension by the method of stationary waves, led to results similar to those obtained by the other two methods. Thus, for example, the cord to which the figures in the preceding table refer was put through the following operations: The fresh cord was brought to  $\Lambda = 5$ . The inter-node was found to be 177 cm. The rubber was now held at this extension for 15 hours. The inter-node was now found to be 193 cm. Hence, it was indicated that the period of repose in question had increased the velocity of propagation in the ratio  $193 : 177 = 1.09$ , and  $E_1$  or  $E_2$  in the ratio  $(193)^2 : (177)^2 = 1.18$ . The cord was then subjected to seven cycles, the upper limit in each case being  $\Lambda = 5$ , and the lower limit gradually approaching in each succeeding cycle to  $\Lambda = 1$ . The inter-node, measured at  $\Lambda = 5$ , fell after each cycle. After the last cycle ( $\Lambda = 5$ ,  $\Lambda = 1$ ) it was 139 cm. After three hours' repose at  $\Lambda = 5$  it had risen to 158, and after six hours' repose to 167 cm.<sup>1</sup>

Kurz<sup>2</sup> measured the modulus by suspending a weight, M, by the lower end of a strip of rubber, the upper end of which was fixed, and then observing the period of oscillation of the weight.

The period of vibration,  $T = 2\pi\sqrt{\frac{LM}{gE}}$ . Bouasse,<sup>3</sup> however, points out the deficiencies of this method. The amplitude of the oscillations ought to be maintained; and to maintain it presents a problem of technique still more difficult than that presented in the dynamical method employed by Bouasse. Phillips,<sup>4</sup> in another connection, has made some observations on the oscillation of a weight suspended by a rubber cord.

*Flattening a rubber sphere.*—Schneebeli<sup>5</sup> has made some observations which are of interest particularly because they suggest

<sup>1</sup> Bouasse notes that the hysteresis observed in  $E_1$  determined by this method is noticeably smaller than when other methods are used. This is not to be regarded as indicating a deficiency in the method. For hysteresis may be regarded as due to a number of different phenomena, which distinguish actual materials from perfectly elastic materials, and which may each have its own hysteresis. Hence, it need not be regarded as astonishing that the amount of hysteresis observed in the determination of  $\epsilon$  by the pendulum differs from that observed in its determination by stationary waves.

<sup>2</sup> *Repertorium*, 1887, **23**, 311.

<sup>3</sup> *Loc. cit.*, p. 190. Cf. also Bouasse, "Sur l'amortissement des trepidations du sol par les suspensions en caoutchouc," *J. de Phys.*, 1904, **3** (4), 511.

<sup>4</sup> *Phil. Mag.*, 1905, **9** (6), 513.

<sup>5</sup> *Arch. de Gen.*, 1886, **15** (3), 534 (*Beibl.*, **10**, 602).

a novel method of determining the elastic modulus (for compression). According to a formula developed by Hertz,<sup>1</sup> when a sphere of an elastic solid is pressed against a rigid plate, the radius of the circle produced by flattening ( $r$ ) is related, for small flattenings, to the pressure being exercised ( $p$ ) as follows:  $r/p^{1/3} = \text{constant}$ . Schneebeli, experimenting with spheres of rubber, found this formula to be satisfied even for considerable flattenings. Thus, with a sphere 52.4 mm. radius pressed against a copper plate by pressures varying from 4.932 to 76.932 kg., the value of the expression  $r/p^{1/3}$  varied from its mean value by less than 4 per cent. Further, Schneebeli points out how Young's modulus can be derived from the magnitude of the flattened circles. In the formula of Hertz:—

$$r = \sqrt[3]{\frac{3p\delta R}{16}}$$

$\delta$  is a constant directly related to Young's modulus. ( $R$  = the radius of unflattened sphere.) For the rubber employed by Schneebeli, the value of 0.164 kg./mm.<sup>2</sup> for the modulus was calculated.

#### THE IMPACT OF RUBBER CYLINDERS

A matter which bears some relations to the question of the velocity of propagation of an impulse through a rubber cord, and to that of the damping of vibrations in rubber, is the impact of two rubber cylinders. According to a phase of elastic theory developed particularly by Saint-Venant,<sup>2</sup> the result of the impact of two rods depends not only on the masses of the rods, but also on their length and on the velocity of propagation of longitudinal waves in them. The actual impact produces a longitudinal wave; and the result of the impact is influenced by the time of return of this wave after it has been reflected by the free end.

Boltzmann<sup>3</sup> endeavoured to confirm this conclusion experimentally. Failing with glass cylinders to find, after impact, differences sufficiently large to be recognized with ease experimentally, he turned to rubber, as a material in which the effect

<sup>1</sup> "Ueber die Berührung fester elastischer Körper," *Fortschr. Phys.*, 1882, I, p. 276.

<sup>2</sup> *C.R.*, **63**, 1108; **64**, 1009, 1192; **66**, 650, 877. The problem of the longitudinal impact of bars has figured rather prominently in the development of elastic theory. Cf. *A History of the Theory of Elasticity*, I. Todhunter and K. Pearson, Cambridge, 1893.

<sup>3</sup> *Sitzungsber. Wien*, 1881, 84 (II Ab.), 1225.

might be expected to be very much larger than in glass; and he ascertained that, in fact, in the case of the impact of two rubber cylinders of equal mass, there was a distinct difference in the result of the impact, depending on whether the cylinders were of equal or unequal lengths. Four cylinders of soft, grey rubber, of equal weight, but of unequal lengths, were prepared. A thin plate of bone, the outer surface of which was rounded, was cemented on to that end of each cylinder which was to take part in the impact. The cylinders were suspended, co-axially, in a horizontal position, pendulum-wise. One of a pair of cylinders under experiment was drawn back from its position of rest by a definite distance,  $H$ , by means of a silk thread; the cylinder was released by burning the thread; and the distance through which the second cylinder was moved as a result of the impact was measured.

Instead of quoting Boltzmann's numerical results, some results of Hausmaninger,<sup>1</sup> a pupil of Boltzmann, who extended the work, may be given. Hausmaninger determined, in addition to the distance through which the second cylinder was moved by the impact ( $S$ ), the distance through which the first cylinder moved back after the impact ( $s$ ). The cylinders were made of fresh, soft rubber. Their masses were equal within 0.5 per cent. Their dimensions were as shown below:—

		Length (without bone plates).	Diameter.	Weight (with attachments).
The shorter cylinders	{ A	198 mm.	20 mm.	69.81 g.
	{ A'	201.3 mm.	20 mm.	69.85 g.
The longer cylinders	{ B	399.5 mm.	14 mm.	70.13 g.
	{ B'	397.0 mm.	14 mm.	70.19 g.

When  $H$  was 100 mm., the results obtained were as follows:—

		Mean.	Extreme figures.
1. Impact of cylinders of equal length, i.e. A striking A'; A', A; B, B'; B', B (12 observations in all).	{ S	84 mm.	83.5-85.5
	{ s	12.5 mm.	10-14
2. Impact of cylinders of unequal length, i.e. A striking B'; B', A; A', B'; B', A'; A', B; B, A' (18 ob- servations in all).	{ S	77.5 mm.	76.5-78.5
	{ s	17 mm.	16-18

It will be observed that the distance to which the struck cylinder is deflected from its position is greater when the two cylinders are of equal lengths, and that, conversely, the distance through which the striking cylinder moves back after the impact

<sup>1</sup> *Sitzungsber. Wien*, 1883, 88 (II Ab.), 768.

is greater than when the two cylinders are of unequal than when they are of equal lengths.

Hausmaninger determined experimentally the magnitude of the period of time for which the actual impact lasts. For this purpose he used a method, depending on the ratio of the stationary and momentary deflections of a galvanometer needle. It appears from the results that the period in question is longer when the cylinders are of unequal than when they are of equal lengths. It is, however, in any case very brief. Further, the period is independent of the distance,  $H$ , through which the striking cylinder is moved to make the impact. Thus:—

TABLE LXVIII

	$H$ , 100 mm.	$H$ , 50 mm.	$H$ , 30 mm.
1. <i>Cylinders of equal lengths.</i>			
A' striking A (secs.)	0'0068	0'0068	0'0069
2. <i>Cylinders of unequal lengths.</i>			
B' striking A (secs.)	0'0111	0'0114	0'0110
A striking B' (secs.)	0'0109	0'0112	0'0112

In view of these figures, which reveal the actual period of contact as extremely brief, Hausmaninger concludes that the formula proposed by Voigt<sup>1</sup> in his treatment of the theory of impacts is not applicable.<sup>2</sup>

The figure obtained by Stefan, by Bouasse and by Exner for the velocity of propagation of longitudinal waves in rubber, is approximately 40 m. per second. When this datum is considered in conjunction with the briefness of the period of actual impact, during which the cylinders can exercise reciprocal action, the theoretical problems presented by the impact of two rubber cylinders would appear to be somewhat difficult. So far as the present writer is aware, the case of the co-axial impact of two rubber cylinders has not been studied further than is mentioned

<sup>1</sup> *Berl. Ber.*, 22 June, 1882; *Ann. der Phys.*, 1883, **19**, 44.

<sup>2</sup> It may be of interest to quote the corresponding figures for glass cylinders, as illustrative of the fact, mentioned earlier, that rubber frequently shows a behaviour different from, or opposed to, the behaviour of other solid bodies. In similar determinations on glass rods of equal mass but unequal length, Hausmaninger (*loc. cit.*) found that (a) the duration of contact, which with glass was very short—in no case more than 0'0007 sec., was not, as with rubber, independent of  $H$ , but became shorter as  $H$  became larger; (b) the duration of contact was longer when the rods were of equal than when they were of unequal lengths; (c) the duration of contact was briefer when the longer rod struck the shorter than when the shorter rod struck the longer one. For data on steel cylinders, vide, *e. g.* Schneebeli, *Ann. der Phys.*, 1871, **143**, 239.

above, either theoretically or experimentally. Other conditions being similar, the result of impact in the cases of different rubber cylinders would be influenced by differences in the elastic modulus of the rubbers in question, and might be successfully related, either theoretically or empirically, to the magnitude of the modulus.

*Impact tests.*—Mention may be made at this point of the employment of impact tests in the evaluation of rubber. Impact tests on rubber have been developed only to a slight extent. Memmler<sup>1</sup> describes a pendulum-impact tester made by L. Schopper. "A rubber disc, 5 to 10 mm. in thickness and 1 sq. cm. in area, is fixed on the face of one of the pendulum hammers. The left pendulum hammer comes, after being released, against the right one. The impact energy absorbed by the rubber disc, and also the surplus energy not absorbed, is indicated by the position of the pointers, which are loosely fixed on the axle of the pendulum and move over a scale." Results with this apparatus have not hitherto been reported. It may be regarded as improbable that it will give results of much value with discs such as those just mentioned. The apparatus would seem, however, to be adaptable to the conduct of impact tests on rubber cylinders, such as are suggested by the observations of Boltzmann and Hausmaninger.

Beadle and Stevens<sup>2</sup> have described some impact tests of a different character. They designate them as impact-tensile tests. In them a single pendulum is used. At the bottom of its fall the pendulum strikes the sample of rubber under examination. The pendulum ruptures the rubber, and as a result loses part of its potential energy. The energy remaining carries the pendulum a certain distance,  $H^0$ , up the other side of the stroke; the highest point reached being indicated by an adjustable pointer. The energy absorbed in rupturing the rubber is then expressed as  $W(H - H^0)$ , where  $W$  is the weight of the pendulum and  $H$  the height from which the pendulum was allowed to fall. The test piece consisted of a small ring. It is not clear as to what tension the samples were under at the moment of impact.

The authors justly point out that impact-tensile tests may be expected to be of value in relation to the employment of rubber in some connections where it is exposed to sudden strains. "Take, for instance, the case of a tyre—especially a solid tyre—meeting an obstacle in the road. In such a case

<sup>1</sup> *Rubber Industry*, 1911, p. 365.

<sup>2</sup> *Ibid.*, 1911, p. 344.

the rubber compound is subjected to a sudden jar, quite unlike the gradually increasing stress put upon it for ordinary strength determinations." It does not appear, however, from the results given by Beadle and Stevens that, as employed by them in the manner just described, an impact test is capable of distinguishing sharply between different rubbers.

#### STRESS-STRAIN RELATIONS ON COMPRESSION

Following the introduction of the process of vulcanization in the 'forties, one of the applications of vulcanized rubber that

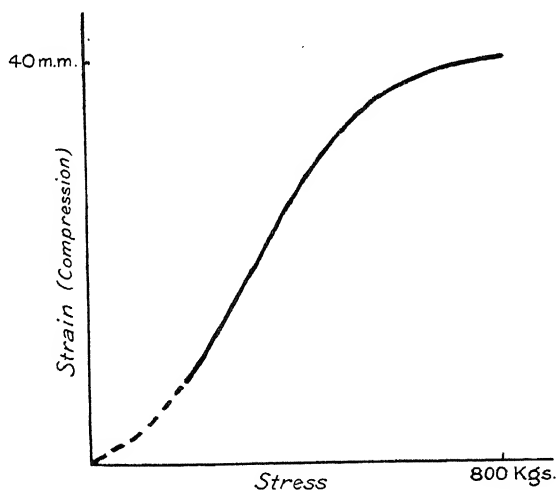


FIG. 12.

first excited interest was its use for the manufacture of buffers for employment on railways. It is, therefore, not unnatural that the first records of quantitative measurements on the stress-strain relations in rubber should refer to the compression of rubber discs arranged as a buffer. Boileau,<sup>1</sup> in 1856, recorded measurements of the amount of compression produced, in rubber which is free laterally, by increasing loads up to a point short of that at which permanent deformation would be produced. The buffer with which Boileau worked was composed of eight rubber discs, separated from each other by discs of iron, 5 mm. thick, and held together by a stem passing through the centre of the discs. The dimensions of the discs were as follows:

<sup>1</sup> C.R., 1856, 42, 933.



thickness, 23 mm.; external diameter, 93 mm.; diameter of central hole, 39 mm. Thus, the total thickness of the rubber of the buffer was 184 mm. The load was applied by weights placed on a lever, the maximum load in the experiment quoted below being 806 kg. Boileau's figures are transcribed in Fig. 12.

It is interesting to observe the general similarity of aspect of this curve to the better-known stress-strain curve referring to extension. It appears that the readiness with which the rubber is compressed increases initially, and then begins to diminish, and, finally, falls very greatly; the curve becomes "flat" in the last stage. This is further seen in the following table, which Boileau gives, showing the amount of compression in mm. (C) corresponding to each increment of 0.2 kg./cm.<sup>2</sup> in the load.

TABLE LXIX

Load (kg./cm. <sup>2</sup> )	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	
C . . . . .	0.66	0.64	0.70	0.80	0.99	1.05	1.04	0.98	
Load (kg./cm. <sup>2</sup> )	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	
C . . . . .	0.90	0.80	0.73	0.70	0.66	0.63	0.60	0.57	
Load (kg./cm. <sup>2</sup> )	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5	14.0
C . . . . .	0.49	0.32	0.20	0.15	0.14	0.13	0.12	0.11	0.10

Boileau recognized the existence of hysteresis on lifting the stress, for he says: "When, starting from 806 kg., I remove the load slowly and progressively from the column, the latter does not recover exactly the corresponding height which it had at each load during the period of compression, but it has returned to its original height when all the load has been removed." He does not, however, record any figures referring to unloading.

Other early observations on the compression of rubber are those of Hovine,<sup>1</sup> Debonnefoy<sup>2</sup> and Werder.<sup>1</sup> The investigations, at a later date, of Heinzerling and Pahl, which, as the first systematic examination of the influence of various compounding ingredients on the mechanical properties of rubber are of considerable historical interest, included compression tests.

Stévant,<sup>3</sup> later than Boileau, made more extensive tests with annular discs of the same kind of rubber as that employed in his stretching experiments, *i. e.* a red rubber, with a specific

<sup>1</sup> Cf. Breuil, *Lects. on Rubber*, 1908, p. 299.

<sup>2</sup> *Soc. Ing. Civ. Mém.*, 1854, p. 86.

<sup>3</sup> *Loc. cit.*

gravity of 1.060-1.065. He subjected such discs to loads increasing by 15 increments from 1500-7000 kg. The first-mentioned load produced a compression of more than one-third of the original thickness, and the last-mentioned, which corresponded to about 100 kg./cm.<sup>2</sup>, of about two-thirds of the original thickness.

The compressions produced by equal increments of load rapidly fell off; the stress-strain curve being evidently asymptotic to the stress axis. The curve was a hyperbola; the thickness,  $t$ , at any load,  $P$ , being expressed as a fraction of the original thickness,  $T$ , as follows, where  $a$  is a constant characteristic of the sample in hand:—

$$\frac{t}{T} = \frac{1}{\sqrt{aP + 1}}.$$

By a series of further tests<sup>1</sup> on discs of varying dimensions it was found that the constant  $a$  was proportional to the thickness of the disc, inversely proportional to the superficial area of the disc, and independent of the other dimensions; so that, introducing a new constant,  $K$ , the relation between the thickness and the load at any point of the compression was

$$\frac{t}{T} = \frac{1}{\sqrt{K \frac{TP}{S} + 1}},$$

where  $S$  = cross-sectional area.

Stévant made no observations on unloading. Stévant's formula does not, the present writer finds, fit Boileau's data. Breuil<sup>2</sup> finds it to be inapplicable to compression tests which he made on some rubber compounds, five in number. Stévant's observations do not cover the first part of the compression; his smallest load, as already mentioned, reduced the thickness of the rubber to less than two-thirds of its original thickness.

Van Heurn<sup>3</sup> has recently made some measurements on compression covering the same portion of the stress-strain curve to which Boileau's figures refer. The stress-strain curves which he obtains are not hyperbolic, but are similar in character to the curve corresponding to Boileau's figures.

*Hysteresis loops.*—Van Heurn gives the stress-strain curve corresponding to unloading after compression. It will be noticed

<sup>1</sup> In these tests only five loads were applied, viz. 2000, 2500, 4000, 5500 and 7000 kg.

<sup>2</sup> *Lects. on Rubber*, 1908, p. 300.

<sup>3</sup> *Meded. Delft*, 1916, p. 429.

(Fig. 13) that not only does the stress-strain curve on compression—at all events up to a compression of 30–40 per cent.—present, as already remarked, a general aspect during the loading phase similar to the general aspect of the well-known stress-strain curve for extension, but that it forms, with unloading, a hysteresis loop reminiscent of the hysteresis loop corresponding to extension and subsequent retraction (*vide* Chap. XVIII). Van Heurn's tests were made on three cylinders, of somewhat mineralized rubber, the composition and vulcanization conditions of which are in two of the cases recorded. The cylinders had

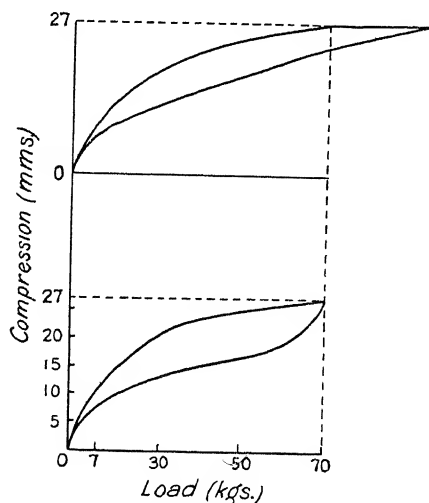


FIG. 13.<sup>1</sup>—Hysteresis loops on compression.

a length of 72 mm. and a diameter of 29 mm. The tests were conducted on a Breuil dynamometer. Two of the autographic records are shown in Fig. 13.

#### TORSIONAL MEASUREMENTS

Mallock<sup>2</sup> measured the rigidity or torsion modulus under no-load of the three samples of rubber mentioned on p. 227. The pieces of rubber, which were of approximately square cross-section and 11.2 in. in length, were arranged vertically, so that the lower end was held fixed, while to the upper end a horizontal

<sup>1</sup> The limit of compression allowed by the apparatus was 27 mm.

<sup>2</sup> *Loc. cit.*

bar, extending 28.4 in. to either side of the axis of the rubber, was attached. The ends of the rubber were held in simple brass clamps consisting substantially of small boxes. Above the bar was placed a divided circle. To one end of the bar two silk threads were attached, one carrying a plumb-bob and the other a small weight. In order to subject the rubber to torsion, the latter thread was pulled to one side; and, from a measurement of the distance through which it was pulled, the torque to which the rubber was subjected was derived.<sup>1</sup>

The following results were obtained. For comparison, the values found for Young's modulus for the same rubbers are given:—

TABLE LXX

Rubber.	Young's modulus (lb./in. <sup>2</sup> ).	Simple rigidity. <sup>2</sup>
Soft, grey (sp. gr. 1.284)	124	65
Red (sp. gr. 1.407)	166	50
Hard, grey (sp. gr. 2.340)	495	158

*Dynamical measurements of rigidity.*—Dynamical measurements of rigidity were also made by Mallock, by removing the weights from the silk threads in the above-described arrangement, and determining the period of oscillation when the rubber was subjected to torsion. The results were similar to those obtained statically, but were not so constant. For both grey rubbers the period of oscillation varied considerably with the arc of vibration, owing partly to the extinction of the vibrations being so rapid.

Hebb<sup>3</sup> examined the variation of the rigidity with extension, using both the statical and the dynamical methods. In applying the latter method, he followed Mallock's procedure, except that the upper end of rubber was fixed and the lower end subjected

<sup>1</sup> The formula used for the calculation of the rigidity by this statical method is  $n = 2Tl/\pi r^4\theta$ , where  $T$  is the torque applied,  $l$  the length of the rubber,  $r$  its radius,  $\theta$  the angle of twist in circular measure.

<sup>2</sup> Mallock suggests that possibly a kind of "grain" in the sheets of soft, grey rubber may account for the fact that it here gives a greater coefficient of rigidity than the red rubber, whereas it gave a smaller Young's modulus. According to elastic theory, Young's modulus should be very nearly three times the torsion modulus.

<sup>3</sup> *Trans. Nova Scotian Inst. Sc.*, 1898-1902, **10**, 273.

to torsion. In applying the kinetic method,<sup>1</sup> it was found that, as in the case of Mallock's experiments, the time of oscillation was noticeably influenced by the magnitude of the angle through which the rubber was twisted, becoming smaller as the angle of twist increased. Graetz<sup>2</sup> has earlier remarked that the period of oscillation was very noticeably dependent on the torsion angle if the latter were above 80°. In his own observations, Graetz used a torsion angle of 40°. And Cantone and Contino<sup>3</sup> has also found that the torsion angle increased more quickly than the torsional force. The angle of twist must be specified in recording results both in the case of the static and in the case of the kinetic method.

The rubber compound used by Hebb contained 60 per cent. of rubber. In the first series of measurements the extension was increased by 13 steps from a length of 35.06 in. to one of 42.11 in., the load being allowed to act at each step for one day before readings were taken. The rubber was then unloaded similarly. It was found both during extension and during retraction that the rigidity first fell, then passed through a minimum, and again rose. Thus, the kinetic rigidity determined from the time of oscillation after a twist of 90° had fallen from 217 (English units) when the length was 35.06 in., to 169 when the length had become 42.11. The minimum was less clearly marked in the figures for statical than in those for dynamical rigidity.

Some observations were then made on the change of rigidity with the continued action of a given load. It was found that the rigidity was at a minimum immediately after the application of a load and increased with time. For steps such as those indicated above, and within similar limits of extension, it was found that the effect of adding a further load after the load already imposed had been acting for one or more days was to produce a marked temporary reduction in the rigidity. A series of measurements of rigidity, with step-wise increase of extension, was therefore made, in which the rigidity was determined immediately after the application of each load. Under these conditions no minimum, such as that in the first series of observations, occurred, but a gradual increase of the rigidity

<sup>1</sup> The formula used for the kinetic method was  $n = 8\pi I/t^2\gamma^4g$ , where  $I$  is the moment of inertia of the stretching weights and  $t$  the time of a complete oscillation.

<sup>2</sup> *Ann. der Phys.*, 1886, **28**, 354.

<sup>3</sup> *Rend. Ist. Lomb.*, 1899, **32** (2), 189 (*Beibl.*, 1899, **23**, 614).

with extension. The increase was, however, slow—from 150 at a length of 34.58, to 169 at a length of 41.44 in.—and it was thought possible that the rigidity might not vary at all with the extension under conditions of continuous loading; the increase found being entirely due to the time effect of the previous increments of load. It would seem probable, however, that there is a real increase of the rigidity with extension, particularly with large extensions. Cantone and Contino found a very marked increase in the rigidity with increase of load. (These last-named authors also investigated torsional hysteresis.)

The relation of the rigidity of rubber to the quality of the raw rubber, and the composition of the "compound" and its state of vulcanization, has not yet been the subject of investigation.

#### THE STRESS-STRAIN CURVE AND THE INTIMATE STRUCTURE OF RUBBER

From a consideration of the stress-strain relations in rubber, which, as was remarked at the beginning of the present chapter, stand in marked contrast to the stress-strain relations in most other materials, several writers have, independently, formed pictures of the intimate structure of rubber, as it refers to its mechanical properties, which have a general similarity. Rubber is pictured as consisting of two parts: <sup>1</sup> a readily-deformable or jelly-like part enveloping or associated with a tenacious part; the steep portion of the stress-strain curve representing predominantly the stress-strain relations of the former, and the flat portion the stress-strain relations of the latter part.

Mallock <sup>2</sup> points out that the great increase in the resistance of rubber to stretching beyond the steep portion of the extension curve "suggests that the structure of the material brings some sort of mechanical stop into action." And he goes on to compare the behaviour of rubber with that of certain mechanical mixtures which consist of an easily-deformable part and a

<sup>1</sup> The work of Bjerken (*Ann. der Phys.*, 1891, 43. *Vide* Chap. XX.) on the analogies between rubber and gelatine in their elastic properties, and in the exhibition of accidental double refraction as a result of mechanical deformation, and the work of L. Schiller (*Ann. der Phys.*, 1911, 35, 931. *Vide* Chap. XX.) on the change in the dielectric constant of rubber as a result of mechanical deformation are suggestive in relation to the question of the structure of rubber. And, like consideration of the stress-strain curve, they indicate a two-component structure.

<sup>2</sup> *Loc. cit.*

tenacious part. It is supposed that when stressed beyond a certain point such mixtures may "firm up" owing to the particles of the tenacious constituent coming into actual contact. Mallock writes as follows:—

"If a lump of putty (chalk and oil) be well rolled or beaten, it will be found to be slightly elastic, but beyond the elastic limit to be easily stretched for a certain distance and then to become almost hard, at the same time the appearance of the surface changes from a smooth, oily character to a dull, granular one.

"The explanation of this case is that the hard particles of the mixture are, in its undisturbed state, separated each from its neighbour by a wall of fluid of finite thickness. When the material is distorted, the particles separate from one another in one direction and approach one another in a direction at right angles to this. As long as this approach merely involves the flow of the intervening fluid, the distortion takes place with comparative ease; but when the approach of the particles brings them in actual contact with one another, the conditions change. There is no longer a store of fluid between, say, the vertical layers of particles which can be drawn in to supply the increased distance between the horizontal layers, and if the strain is augmented it must simply imply either a distortion of the hard particles themselves or an increase of volume of the whole mass.

"The latter is what happens in the case just mentioned, the dull surface being the result of the fluid being sucked or rather pushed inwards by the atmospheric pressure to supply the extra volume required, thus leaving the surface comparatively dry."

Cheneveau and Heim,<sup>1</sup> from a consideration of the character of the rubber stress-strain curve, were led to remark: "One could imagine that the molecular constitution of vulcanized rubber is such that the rubber acts during the extension process like a substance whose molecules are formed of a tenacious nucleus of low extensibility and a soft, non-tenacious, highly extensible envelope. . . . The initial elongation of the rubber would correspond to the extension of the enveloping matter alone; the middle elongation (medial portion of the extension curve) would correspond to the simultaneous and uneven extension of envelope and nucleus under the increasing stresses, and the last elongation, which comes before the breaking-point, would correspond to the very limited deformation of the substance of the nucleus under heavy stresses."

<sup>1</sup> *C.R.*, 1911, 152, 320; *Rubber Industry*, 1911, p. 329.

Fessenden,<sup>1</sup> who states that the elasticity of organic substances, such as rubber and jelly, cannot have the same causes as cohesion and elasticity in metals—which he regards as due to the direct attraction of electrostatic charges—remarks that he has found it often to be the case that, when two substances are mixed together but not dissolved, the resulting product is much more elastic than either of its components. He states generally that “all substances which are highly elastic are, as actual observation shows, made of two or more components in a state of mixture.” He goes on: “In the case of rubber, for instance, we have for its components . . . two substances: one, which is somewhat like horn—hard, elastic, but possessing very little extensibility;<sup>2</sup> and another substance, like a very thick molasses, or a soft asphalt, or stearin pitch. Neither of the two has anything like the elasticity of rubber itself. . . .

How this mixing can confer such great elasticity is seen from the following considerations: Suppose we have a copper ball filled with a practically incompressible fluid, such as water,

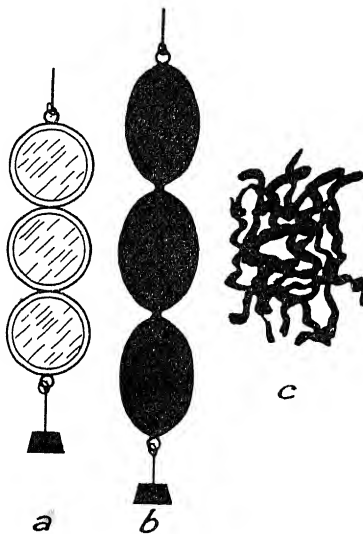


FIG. 14.

Fig. 14, *a*. Let the radius of the sphere be 1 cm. Suppose I pull it out until it forms an ellipsoid, and until its major axis is 3 cm. long, Fig. 14, *b*. Then, on the assumption that the

<sup>1</sup> “Some Recent Work on Molecular Physics,” *J. Franklin Inst.*, 1896, **142**, 187 (particularly pp. 207–9).

<sup>2</sup> In an earlier paper (“The Laws and Nature of Cohesion,” *Science*, 1892, **20**, 48; 1893, **21**, 113; *Chem. News*, 1892, **66**, 206; 1893, **68**, 294) Fessenden would appear to identify the hard, elastic component with the portion of the raw rubber insoluble in rubber solvents. Such identification would not, however, seem to be acceptable. The characteristic rubber stress-strain curve, on a consideration of which the two-component view of rubber is based, is obtained, not with raw rubber, but only with vulcanized rubber. And the latter is wholly insoluble in rubber solvents. Further: the portion of raw rubber which is insoluble in rubber solvents, and which, at the date of Fessenden’s paper, was regarded as an insoluble form of caoutchouc, has been shown by Spence to consist essentially of protein.



thickness of the skin remains constant, we have an increase of area of 13 per cent., or a linear elongation of 6 per cent. But as the skin is stretched, it contracts in thickness, so that, for this reason, a less linear extension is needed, in this case only about 1.5 per cent. Thus we get an elongation of 50 per cent., at the expense of only 1.5 per cent. elongation of the material which does the stretching.

Now, it is fairly easy to see that a lump of the tar-like component of india-rubber, surrounded by strings of the horn-like substance, would give a similar effect; for the strings may be considered as forming the walls of the sphere, and the viscous substance as taking the place of the water, Fig. 14, *c*. Thus we may have a very great extension of an india-rubber strip, with but little actual extension of the horny substance and none of the other component." Further, the extension would be asymptotic in the case of the ball, as it is in the case of rubber.

As mentioned in Chap. XX, Fessenden sees in this view of the structure of rubber an explanation of the Joule Effect. He puts the matter as follows: "What will happen if I suddenly pull out the water-filled ball? I compress the water, and it will heat. If I leave it extended for some time, and then let it contract, it will cool. Exactly the same phenomena can be observed in india-rubber. . . . Again, what would happen if, whilst the ball were stretched, I heated it? Evidently the water would expand, and, in expanding, would force the ball to return to its original spherical shape. Here we have a curious paradox—contraction caused by expansion—and this phenomenon is exactly duplicated in the case of rubber."

## CHAPTER XI

### TECHNIQUE OF TENSILE TESTS

IN addition to questions of technique similar to those presented by the tensile testing of other materials, rubber presents, in regard to tensile tests, special questions, which do not arise or are less conspicuous with other materials. Some of the general questions which the technique of tensile tests on rubber presents will be discussed in the present chapter. The discussion will make clear the importance of strict standardization in the conduct of mechanical tests on rubber.

#### GRIPS

The problem of gripping—for the purpose of conducting tensile tests—material so extensible as high-grade rubber offers peculiar difficulties, such as are not encountered in the tensile testing of other materials. The special problems of technique which the tensile testing of rubber has presented have centred largely round the question of gripping specimens of high-grade rubber which it is proposed to stretch to the breaking-point.<sup>1</sup>

The difficulty of actually gripping rubber specimens which were to be taken to great extensions was early recognized; and test pieces, provided with loops or in the shape of rings, which could be supported without actually gripping them at all, were used. Villari, who conducted the earliest published investigation into the rubber-stretching curve (1869), made loops at the ends of the test strips; each end was bent over to form a loop, and, while the strip was stretched strongly, was bound with waxed twine. Mallock (1889), another early experimenter to take strips of high-grade rubber to the breaking-point, also provided the strips with loops. Stévant<sup>2</sup> was the first to introduce the use of rings.

<sup>1</sup> For an account of some of the early troubles in connection with gripping the test piece, see Frank's account of the development of the Schopper instrument, *Rubber Industry*, 1908, p. 289.

<sup>2</sup> Stévant's work was originally published in the *Bulletin du Musée de l'Industrie* (Belgium) in 1870, but became generally accessible only in 1888, when it was published as a monograph. The paper by Jenatzy, *Bull. de l'Association des Gaziers belges*, 1881-2, p. 20 (*Proc. Inst. Civ. Eng.*, 1882-3, 71, 520) is, Stévant states, a plagiarism.

In Stévant's experiments the rings were suspended vertically from a hook, and the loading pan was attached by means of another hook. The extension was read between gauge marks. In a testing machine of the horizontal type, described later by Beadle and Stevens,<sup>1</sup> also, rings are held between hooks. In the beautifully constructed Schopper machine the supports over which the rings pass consist of rotating pulleys; the intention being to avoid the crushing effect at the point of support, which occurs when the supports consist of hooks or stationary pulleys.

It may be admitted that, confining attention to the problem of holding the test piece to the point of rupture, the use of rings passing over rotating pulleys solves the problem more easily and satisfactorily than any method of actually gripping a test piece. The problem of holding the test piece is, however, intimately bound up with the question, discussed more fully a little later, of the most advantageous *shape* in the test piece. Grips are now available which will hold straight test pieces up to the breaking-point; although, as will be pointed out, they have drawbacks in regard to the measurement of elongation.

The Materialprüfungsamt made extensive tests with straight test pieces.<sup>2</sup> Some of the test pieces were of the same width throughout their length, but most had heads, either three times or five times as wide as the middle portion. The heads of the test pieces were held in clamps, which had furrowed faces. As the thickness of the rubber diminished during stretching, the clamps were gradually tightened, so as to maintain their pressure on the specimen. The tests covered six different kinds of rubber. Satisfactory breaks were obtained for all specimens of the five less extensible kinds;<sup>3</sup> but, in the case of the kind representing the highest grade examined,<sup>4</sup> without exception the specimens broke, across the head, in the grips. The present writer's experience is in agreement with the above results. Working with corrugated grips of the above type, on a cloth-testing machine, and using dumb-bell shaped test pieces of high-grade rubber, it was invariably found that the specimens broke in the grips.

It may safely be stated that clamps of the above-mentioned or any other ordinary type, employed in the ordinary way, will not

<sup>1</sup> *J. Soc. Chem. Ind.*, 1909, **28**, 1111.

<sup>2</sup> Memmler and Schob, *Mitt. Prüfungsamt*, 1909, **27**, 173.

<sup>3</sup> The best two of these five specimens gave the following mean figures: Material IV:  $P_B = 0.939$ ;  $L_B = 498$ ; Material V:  $P_B = 0.705$ ;  $L_B = 595$ .

<sup>4</sup> Mean figures for this rubber as found from ring tests were:  $P_B$ , 1.243;  $L_B$ , 928.

hold rubber specimens of the highest grade to the breaking-point, even when their faces are scored or furrowed as may suggest itself.

A type of grip introduced by the Bureau of Standards avoids severe punishment in the grips and allows good breaks to be obtained on straight specimens. In this grip the specimen is held between a flat back surface and a number of thin cylindrical discs mounted eccentrically on a pin. The discs act independently; and the grip tightens automatically as the specimen is reduced in thickness.

The grips on the Scott testing machine are similar to those of the Bureau of Standards, except that, instead of a series of discs, a solid roller, with a handle attached by which the pressure on the specimen can be increased, is employed.<sup>1</sup>

The present writer is of opinion that grips such as those of the Bureau of Standards succeed in holding the rubber where ordinary grips fail, not so much on account of the actual gripping effects of the discs produced by their pressure on the rubber against the back of the grip, but, rather, on account of the fact when, owing to the extension, the rubber below the grip and that actually in between the discs and the back of the grip has been reduced in thickness, the rubber which projects above the line of the discs remains unextended and forms a "bank," which, like the head of a nail, prevents the test piece being dragged out of the grips.

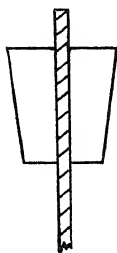
The writer has found that simple, sliding wedge-grips will hold straight test pieces of the highest grade rubber, *if the ends of the test piece project through the grips*. If the ends of the test piece fall in between the grips, the specimen readily draws out, even if the grips are increased in length or are scored in any way that may suggest itself. The condition that causes the grips to hold is the presence of a "bank"<sup>2</sup> of rubber above them. The initial position of the rubber is indicated in Fig. 15 *a*. The condition of affairs after the specimen has been loaded is indicated by the diagram, Fig. 15 *b*.

The wedges slide in a horseshoe-shaped frame. The upper inside edges of the wedges are slightly rounded off. The bank acts in two ways: (*a*) it ensures that the wedges shall travel

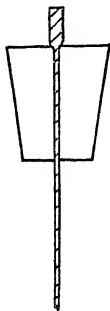
<sup>1</sup> Kratz and Flower (*Chem. Met. Eng.*, 1919, 20, Apr. 15) mention incidentally that several highly extensible specimens ( $L_B$  900 or more;  $P_B$  0.871 or more) tested on a Scott machine "were pinched through by the clamps of the testing machine before the point of rupture or break was reached."

<sup>2</sup> The term "bank" is used here because it is a familiar one in the rubber industry; the cylinder of rubber massed up between the rolls when operations are being conducted on the mixing mills being known as a "bank."

down in the frame as the rubber thins out, and so maintain their pressure on the rubber; (b) being thicker than the distance between



A



B

FIG. 15.

the wedges, it acts like the head of a bolt, and thus prevents the rubber from being drawn through the grips.<sup>1</sup>

#### SHAPE OF THE TEST PIECE. THE RING AND THE DUMB-BELL

The question as to the most suitable shape in the test piece has resolved itself into a discussion of the relative advantages of rings and straight (dumb-bell shaped) test pieces.

It may be remarked first that strips with parallel sides, *i. e.* of uniform width throughout their length, do not give the full breaking figures. This was shown in the tests of Memmler and Schob.<sup>2</sup> In the case of all the rubbers tested, with one exception, strips with parallel sides failed near or in the grips and gave breaking figures much lower—in some cases more than 50 per cent. lower than those given by any of the straight test pieces with widened ends.

It is necessary in the case of straight test pieces that the strips shall have widened ends. Provided that the curve of the shoulder connecting the widened ends with the middle part of the test piece is not too abrupt, it does not appear to matter seriously, for the purpose of getting a break in the proper position, what are the exact dimensions of the test piece. The tests of Memmler and Schob included five different shapes, the width of the middle part being in each case 8 mm., the width of the end varying from 24 to 50 mm., and the length of the parallel middle part varying between 10 and 50 mm. It did not appear, among these shapes, that the breaking figures were influenced in any recognizable direction by the proportions of the test piece. The test piece which is recommended by the Bureau of Standards

<sup>1</sup> It is of interest to note that Bouasse (*Ann. Fac. de Toulouse*, 1904, 6 (2), 283), in whose experiments the limit of length was 700–800 per cent., found that he could avoid rupture due to punishment in the simple clamps, which he used for gripping his specimens, if the portion to which the clamp was to be applied were drawn out greatly at the moment of applying the clamp. It would seem probable that the effectiveness of this artifice depends on the presence of a "bank" above the clamping surface.

<sup>2</sup> *Mitt. Prüfungsamt*, 1909, 27, 214.

and is very generally used in rubber-testing laboratories in America has the dimensions shown in Fig. 16.

In its essentials the question as to whether the ring test piece or the straight test piece is preferable is the question as to which form of test piece allows of (a) the stress at the breaking-point, (b) the strain at the breaking-point, (c) the relation between stress and strain during the course of the stretching being measured most accurately and conveniently.

(a) *Measurement of breaking stress.*—1. As mentioned in connection with the question of grips, rings are incontestably more convenient to hold to the breaking-point.

2. Owing to the unequal distribution of stress across the section, rings do not give the true breaking stress for the rubber of which they are composed. This point is carefully discussed in the Circular of the Bureau of Standards on the testing of rubber goods.<sup>1</sup> It is clear that, when a ring passing over two pulleys is stretched by separating the pulleys further from each other, the rubber forming the inside portion of the ring will be stretched to a greater extent than that forming the outside portion, and, consequently, that the stress at the inner surface will be greater than that at the outer. Now the elongation which is actually measured—represented by the distance between the pulleys—is the elongation of the inside of the ring; and the stress which is actually measured is the average stress over the cross section of the ring.

If  $t$  = the initial thickness of the ring;

$l_1$ , the initial length measured inside the ring;

$l_2$ , the initial length measured outside the ring;

$L_1$ , the length at the breaking-point inside the ring;

$L_2$ , the length at the breaking-point outside the ring;

$E_1$ , the percentage elongation at the breaking-point of the inside of the ring, i. e. the quantity measured automatically on the dynamometer;

$E_2$ , the percentage elongation of the inside of the ring at the breaking-point;

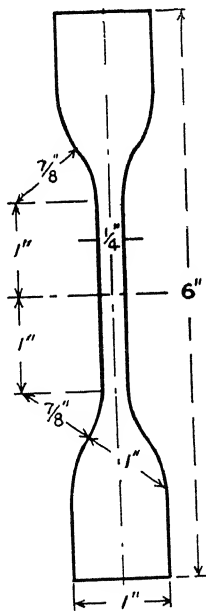


FIG. 16.<sup>2</sup>—Dumb-bell shaped test piece.

<sup>1</sup> Circular of the Bureau of Standards, No. 38, 3rd. edit., 1915.

<sup>2</sup> Where tests are to be made on the Bureau of Standards' dynamometer, and the rubber in question is a high-grade, highly extensible one, the middle part of the test piece is made 1 in. and not 2 in. as represented in this figure.

then, assuming for simplicity that the extensibility of the rubber is the same in all directions, it can readily be shown that—

$$E_2 = E_1 \cdot \frac{l_1 L_1 \pi t \sqrt{\frac{l_1}{L_1} - l_2}}{l_2 (L_1 - l_1)}$$

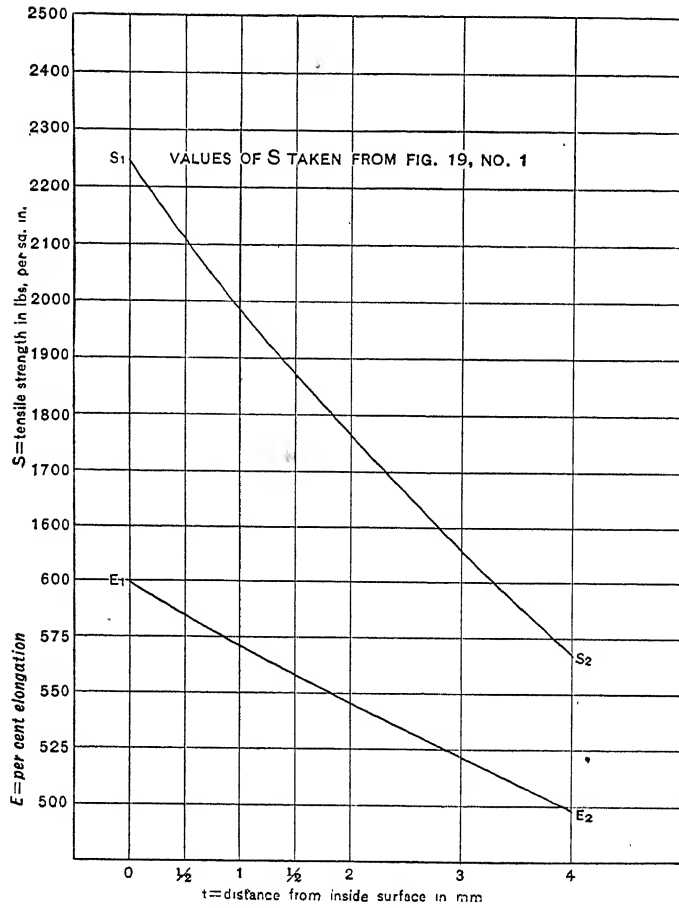


FIG. 17.—Variation in stress and strain from the inside to the outside of a ring.

This relation is a linear one and approximately  $E_2 = 0.83E_1$ . From the above equation it follows that the decrease in percentage elongation is approximately uniform from the inside to the outside of the ring. The decrease for a given specimen for  $E_1 = 600$  per cent., and  $l_1 = 70$  mm. and  $t = 4$  mm. is shown in Fig. 17.

The relation between stress and elongation is practically a linear one for values of the elongation near the breaking point; hence the decrease in stress from the inside surface of the ring to the outside surface may be assumed to be uniform. The decrease is shown in Fig. 17 for the values taken from the stress-strain diagram for Sample No. 1, Fig. 19 (p. 271).

If  $S_1$  = the stress at the inside surface at rupture, *i. e.* the true tensile strength corresponding to the elongation,  $E_1$ , which is measured;  
 $S_2$  = the stress at the inside surface, *i. e.* the stress corresponding to the elongation,  $E_2$ ;

then the average stress,  $S$ , over the cross section, which is the stress measured, will be  $\frac{S_1 S_2}{2}$ , *i. e.*  $\frac{S_1}{2} \left( \frac{S_2}{S_1} \right)$  approximately.

Now, since the ratio  $\frac{S_2}{S_1}$  varies for different rubbers, being larger for high-grade rubbers than for compounds of poor quality,  $S$ , the tensile strength actually measured, is, not only less than, but does not bear a constant relation to  $S_1$ , the tensile strength actually corresponding to the measured elongation,  $E_1$ . Actual tests by the Bureau of Standards showed rings as giving figures in general 10 per cent. or more lower than straight pieces (cf. Table LXX).

It should, however, be pointed out that the Bureau of Standards' tests do not include any rubber of the most extensible type, *i. e.* pure gum compounds giving elongations round 900 per cent. and breaking loads round 2000 lb.-in.<sup>2</sup>.

The Materialprüfungsamt's tests may be considered in general as indicating higher breaking stresses in straight pieces than in rings. The best specimen here in question gave mean breaking figures of approximately  $P_B: 1:00$ ,  $L_B: 500$ .

Both the Bureau of Standards' and the Materialprüfungsamt's investigations covered only a limited range of rubber compounds. It will be observed from Fig. 18 (p. 269) and from Table LXXI that only one rubber of the most highly extensible class, viz. Material I, Fig. 18, was included in these investigations. Since experimental testing in scientific work deals largely with pure gum compounds, such tests on technique made with more particular reference to pure gum compounds would be welcome.

3. The question of a possible "grain" in vulcanized test pieces arises in the present connection. In Memmler and Schob's work with straight test pieces the tests were in every case made both on a test piece cut in the direction of the calender and a piece cut at right angles to it. No definite connection, however, between the direction of the piece with reference to the calender and the breaking figures could be recognized in the results.

The Bureau of Standards, however, conclude that test pieces cut longitudinally to the calender direction exhibit a greater breaking stress and smaller elongation than pieces cut at right angles to it. The following table gives the results for the six different rubbers examined. Sample 5 is an exception to the



general conclusion. Each figure represents the average of 5-15 tensile tests.

TABLE LXXI

No. of rubber sample. <sup>1</sup>	1.	2.	3.	4.	5.	6.
$P_B$ (lb./in. <sup>2</sup> ) :—						
Straight specimens—						
Longitudinal (L) . . . . .	2730	2070	1200	1850	690	880
Transverse (T) . . . . .	2575	2030	1260	1700	510	690
Ring specimens (R) . . . . .	2140	1690	1060	1520	510	730
R/L . . . . .	0.78	0.82	0.88	0.82	0.74	0.83
R/T . . . . .	0.83	0.83	0.84	0.89	1.00	1.06
$L_B$ :—						
Straight specimens—						
Longitudinal . . . . .	730	740	580	510	420	405
Transverse . . . . .	740	770	655	560	380	415
Ring specimens . . . . .	735	775	625	535	385	420

If the stress-strain curves for L, T and R specimens are drawn out, with strains as ordinates, it is found—most clearly in the case of the higher grade specimens, Nos. 1 and 2—that the curve for the T specimen lies above the corresponding curve for the L specimen, and that the curve for the R specimens tends to lie above that for the corresponding T specimen (*vide* Fig. 19). In confirmation of the view that the rubber specimens were stronger longitudinally than transversely, it is noted that the ring specimens showed a tendency to rupture along a line which had been drawn on them to represent the longitudinal direction. The existence of such a tendency indicated that the sheets were strongest longitudinally. It may be remarked, although the point is not specifically noted in their paper, that the rings specimens in Memmler and Schob's tests showed a similar tendency.<sup>2</sup>

It seems probable, then, that vulcanized rubber is stronger in the direction of the calender than in the direction at right angles to the direction of passage through the calender; although, it

<sup>1</sup> The rubbers, 1, 2, 3, 4, 5, 6, dealt with in the Bureau of Standards' tests had specific gravity as follows: 1.64, 1.63, 1.62, 2.22, 2.00. They gave the following analytical figures :—Ash: 53.3 (Barytes, 15.4), 49.6, 57.0 (Barytes, 21.9), 68.9, 66.0; total sulphur (cor.): 2.1, 8.3, 4.1, 4.7, 7.0; free sulphur: 0.7, 3.7, 3.0, 1.7, 1.5; acetone extract (cor.): 2.1, 2.0, 1.7, 1.6, 4.9 per cent. (This information is derived from Wormley, *Rubber Industry*, 1914, 246).

<sup>2</sup> This may be gathered from an examination of the sheets of photographs of broken test pieces which accompanies Memmler and Schob's memoir.

should be stated, the mass of evidence is not as large as could be wished.

If the existence of a "grain" in the rubber to be tested is accepted, it clearly has a bearing on the relative merits of ring and straight test pieces. Straight test pieces can be cut with the grain or across it as desired, and, hence, maximum or minimum figures or both can be secured as desired. Rings give only figures corresponding to rupture along the grain. Memmler and Schob urge that, for the purposes of most ordinary testing work, this circumstance need not be regarded as a serious disadvantage of rings. They urge that it is exactly the strength of the material in its weakest direction that the manufacturer is interested in knowing in regard to a given rubber.

(b) *Measurement of elongation.*—The elongation can undoubtedly be measured with greater accuracy and convenience in the case of rings than in the case of straight test pieces. The length of the ring at any time is given by the distance between the grips; but, owing to slipping in the grips, the length of straight test pieces is not given by the distance between the grips. Even though the grips are successful in holding a straight test piece to the break, there is in the types mentioned above always some movement of the rubber through them.

Van Rossem<sup>1</sup> records tests with the Breuil dynamometer—a testing machine in which the elongation is recorded autographically as the distance between the grips. The elongations thus recorded were compared with the elongations measured directly between two gauge marks placed on the middle portion of the dumb-bell pieces under test. It was found that there were serious differences between the two values for the elongation thus obtained. Van Rossem attributes the differences to imperfect gripping leading to part of the rubber working itself out of the grips.

In the case of straight test pieces the elongation is determined by measuring the distance between two gauge marks inscribed on the middle portion of the piece. Memmler and Schob's tests show that the distance apart at which these marks are drawn does not affect the result provided that the marks do not infringe at all on the heads. To measure elongations by means of two gauge marks involves following simultaneously two lines both of which are moving. This makes the accuracy and convenience with which elongations can be measured very much less in the case of

<sup>1</sup> *Meded. Delft*, 1916, p. 455; *Delft Communics.*, p. 148.

straight test pieces than in the case of rings. Also: in the case of ring test pieces the distance at which the grips are apart when rupture occurs gives the breaking length of the test piece; in the case of straight test pieces no such convenient record of the breaking length is obtained.

(c) *Measurement of stress-strain relations throughout testing.*—

The necessity for measuring the elongation between moving gauge marks makes it difficult to secure a continuous record of the strain, and thus of the stress-strain relations during the course of the stretching, in the case of straight test pieces. And in fact the widely used Bureau of Standards' dynamometer, which is chiefly used for straight test pieces, makes no attempt to secure a graphic record of stress-strain relations throughout the test. The Breuil dynamometer has an autographic arrangement, but the elongations recorded are the distances between the grips, and, as already mentioned, was found by Van Rossem to be unreliable.<sup>1</sup>

The Schopper machine, employing ring test pieces, has in recent models an attachment giving an autographic stress-strain record throughout the test.<sup>2</sup>

The whole tendency of recent experience in rubber testing is, as may be judged from subsequent chapters in this volume, to emphasize, as against the former almost exclusive concern with the breaking-point figures, the importance of the whole stress-strain diagram.

*Summary.*—For accurate measurements of stress and strain in rubber specimens it must be concluded that a machine, such as the Schopper, using ring test pieces, is more satisfactory than a machine, such as the Bureau of Standards machine, using straight test pieces. The most weighty objection to the ring test piece is undoubtedly the fact that it does not give the full breaking stress strictly. But, where rubber samples are to be compared

<sup>1</sup> The Scott machine has an autographic attachment. The present writer, however, has no information as to how successful it is.

<sup>2</sup> Other testing machines which have been described are the machines of Breuil (*Le Caoutchouc*, 1907), Beadle and Stevens (*J. Soc. Chem. Ind.*, 1909, **28**, 1111), Schwartz (*J. Inst. Elec. Eng.*, 1910), Olsen (*Proc. Amer. Soc. for testing materials* 1910, **10**, 588), Cheneveau and Heim (*J. de Phys.*, 1912, **2**, (5), 535). The latter is, with some justice, criticized elsewhere (*vide Le Caoutchouc*, 1914, **11**, 8429, 8561).

A number of machines for tests of a more special character have been introduced and in some cases have found a limited use. Such are machines for abrasion tests (*cf. Mitt. Prüfungsamt*, 1912, **30**, 139), for duration tests, for indentation tests, for compression tests, for impact tests (for all these, *vide Memmler, Rubber Industry*, 1911, 357 *et seq.*), for a rebounding test (*cf. Breuil's "Elastometer," Le Caoutchouc*, 1908, **5**, 2186). Breuil also describes an "Elastodurometer" (*loc. cit.*).

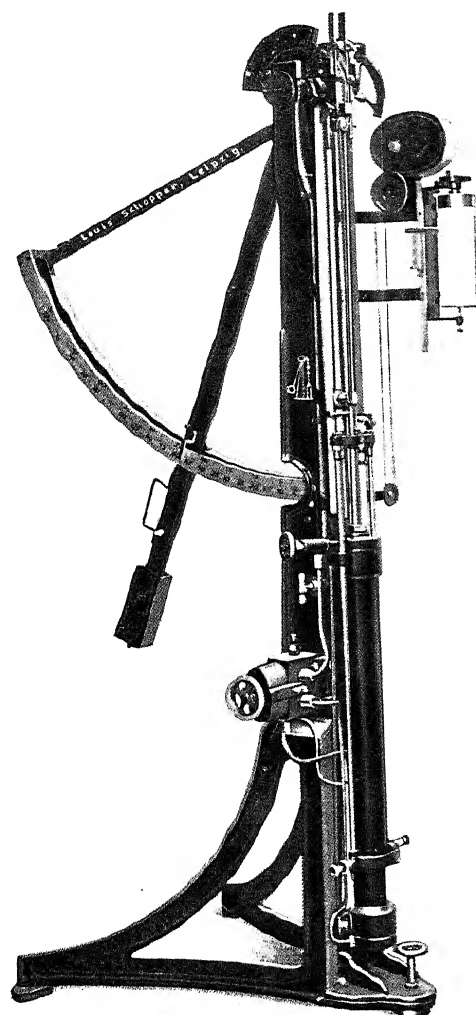


PLATE VII. Schopper's Tensile Testing Machine.

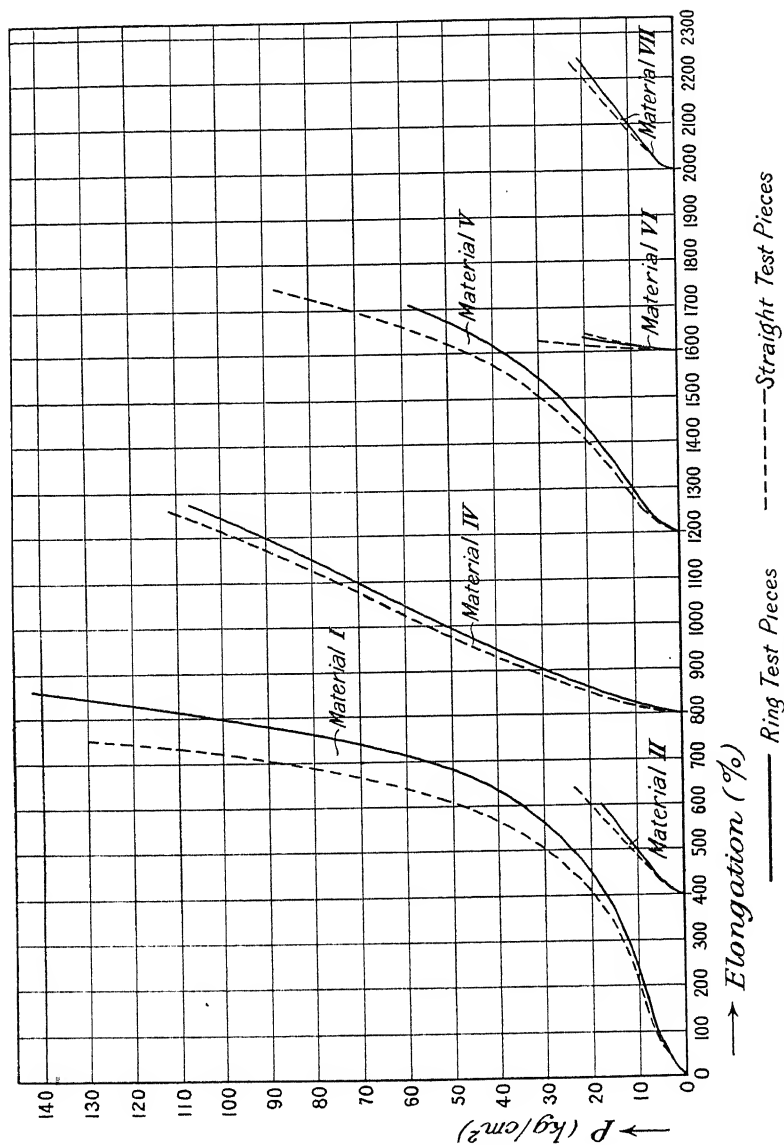


FIG. 18.1.—Stress-Strain Curves of Six Rubbers.

<sup>1</sup> The figures for the straight specimens are the mean of figures for specimens cut across and along the calender, except in the case of Material VI. In the case of this material the curves of straight test pieces cut parallel to and cut across the calender are shown separately in the figure, to the left and to the right respectively. Further reference is made to this figure elsewhere (p. 223).

in compounds of the same type, this objection is not really so serious as might at first appear; and, provided the ring test pieces are of the same dimensions, the results can be accepted as quite satisfactory for all purposes of comparison.<sup>1</sup>

#### SHAPE OF THE TEST PIECE AND POSITION OF THE STRESS-STRAIN CURVE

It was found by Memmler and Schob<sup>2</sup> that for all the rubbers examined by them the stress-strain curve, as plotted from observations from straight pieces, lay below the corresponding curve plotted from observations on rings, *i. e.* that the extension observed under a given load was smaller in the case of a straight test piece than in the case of a ring.<sup>3</sup> This is seen from Fig. 18, taken from these authors.

The tests made by the Bureau of Standards<sup>4</sup> confirmed this result. The following figure, referring to the two most extensible of the samples examined (Samples 1 and 2, Table LXXI), may be reproduced.

In this figure the results on straight specimens cut longitudinally and cut transversely are shown separately (cf. p. 266).

#### DIMENSIONS OF THE TEST PIECE

All investigations agree that the *length* of the test piece is without influence on the results obtained. The question, relative to the dimensions of the test piece, which demands discussion is that of the influence of the *cross section* of the test piece on the tensile results. Stévant, working with rings (of a red rubber of sp. gr. 1.06), ranging in cross section from  $9.2 \times 11.1$  mm. to  $5.0 \times 5.1$  mm., concluded that the elongation produced by equal loads per unit cross sectional area was independent of the cross section. Schwartz,<sup>5</sup> working with rubbers "containing 88 and 66 per cent. Para" in the form of parallel-sided strips,  $\frac{1}{16}$  in. thick and of widths ranging from  $\frac{1}{8}$  to  $\frac{3}{4}$  in., came to a similar conclusion. The

<sup>1</sup> It would seem not impossible that a test piece could be developed which would combine the advantages both of rings and of straight pieces.

<sup>2</sup> *Loc. cit.*, p. 211.

<sup>3</sup> In the former case the extension was measured between gauge marks; in the latter case it was measured on the Schopper machine, as the distance between the pulleys over which the inner surface of the ring passes.

<sup>4</sup> *Circular of the Bureau of Standards*, No. 38, 3rd edit., 1915.

<sup>5</sup> *Jour. Inst. Elec. Eng.*, 1910, 44, 693.

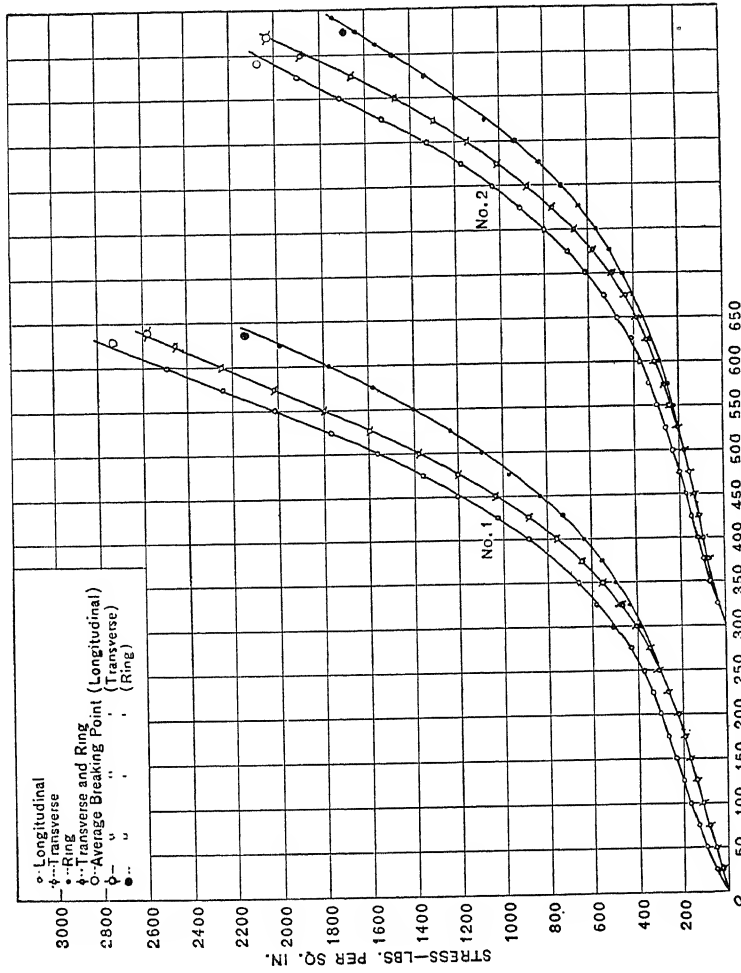


Fig. 19.<sup>1</sup>

<sup>1</sup> For further reference to this figure, *vide* p. 223.

maximum elongation employed in the observations was 400 per cent.

Breuil<sup>1</sup> worked, like Stévant, with rings stretched between hooks. The rings were cut of different widths (10.8, 20, 29, 40, 60 mm.) from rubber tubing. It was concluded that for equal extension the load per unit cross sectional area was almost the same. It was clear, however, that in the case of the wider rings (40 and 60 mm.) the values for the breaking stress were smaller than in the case of the narrower rings.

In the investigations of the authors just mentioned the maximum extensions at which observations were made was comparatively low. The Bureau of Standards,<sup>2</sup> working with straight test pieces with widened ends (cf. Fig. 16), concluded as follows: "As in other materials, there is a tendency for small test pieces to develop higher unit values than large ones. Complete data on this subject are not at hand, but it is thought that test pieces one-fourth inch and one-half inch wide will show, in general, but little differences in ultimate elongation, but an appreciable difference in tensile strength for high-grade (rubber) compounds." This apprehension is verified by Memmler and Schob's results, which are described below. Results reported for five rubbers by the Bureau of Standards are as follows:—

TABLE LXXII

Rubber sample	M-4 Cover.		M-3 Tube.		G-19 Tube.		G-19 Cover.		M-5 Tube.	
Width of piece (ins.)	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$
P <sub>H</sub> (lb./in. <sup>2</sup> )	1565	1455	2160	1955	1025	955	735	690	2490	2060
L <sub>B</sub>	625	615	680	670	450	440	355	350	715	675

The most extensive investigation into the influence of the cross section of the test piece on the magnitude of the breaking figures is that conducted with ring test pieces by Memmler and Schob.<sup>3</sup>

In the first instance rings of 2, 4 and 6 mm. breadth were compared in the case of four different rubbers. The internal diameter of the ring was in each case 44.6 mm. and its thickness 4 mm. In the following table the results are shown.

<sup>1</sup> *Le Caoutchouc*, 1904, p. 56.

<sup>3</sup> *Mitt. Prüfungsamt*, 1911, 29, 198 et seq.

<sup>2</sup> *Loc. cit.*



TABLE LXXIII

a.  Material.	b.  Breadth of ring (mm.).	c.  P <sub>B</sub> .	d.  L <sub>B</sub> .	e. f.	
				Relative values (mean = 100).	
				P <sub>B</sub> .	L <sub>B</sub> .
I . . . {	2	1.589	908	127	100
	4	1.177	906	94	100
	6	0.974	909	78	100
II . . . {	2	0.189	282	103	98
	4	0.188	293	103	104
	6	0.172	283	94	98
Va . . . {	2	1.058	711	109	99
	4	0.971	724	100	100
	6	0.875	728	90	101
VIIa . . . {	2	0.252	287	96	95
	4	0.273	303	104	103
	6	0.260	299	100	102

An examination of the data in the above table makes it clear that, while variation in the breadth of the ring is without serious influence on the breaking stress in the case of low-grade rubbers (Materials II and VII), it has a great influence on the breaking stress in the case of high-grade rubber. The influence of the breadth of the ring appears to be greater, the higher the grade of the rubber.<sup>1</sup> In the case of Material I, which represents a rubber of high extensibility and good strength, reduction in the breadth of the ring from 6 to 2 mm. increases the breaking stress per unit cross sectional area by more than 60 per cent. In the case of Material Va, which represents a less extensible rubber, the increase is almost 20 per cent.—an increase, it may be noted, similar to that shown by the sample in the last column of Table LXXII. In the case of none of the rubbers is the length at break seriously influenced by the breadth of the ring.

In a further and more extensive series of observations, a larger

<sup>1</sup> With reference to this point, Memmler and Schob remark as follows: "Die Tatsache, dass gerade die dehnbaren Gummisorten die grössere Beeinflussung ihrer Bruchfestigkeit durch die Probeabmessungen erfahren, während die Bruchdehnung unbeeinflusst bleibt, legt die Vermutung nahe, dass hier Oberflächenspannungen eine Rolle spielen, denen Materialien mit grossem Formänderungsvermögen mehr ausgesetzt sein werden als solche mit geringerem" (cf. p. 473).

number of combinations of breadth, thickness and internal diameter were examined, all three dimensions being varied. The results are best represented graphically, as in the diagrams in the following figure, given by the authors in question.

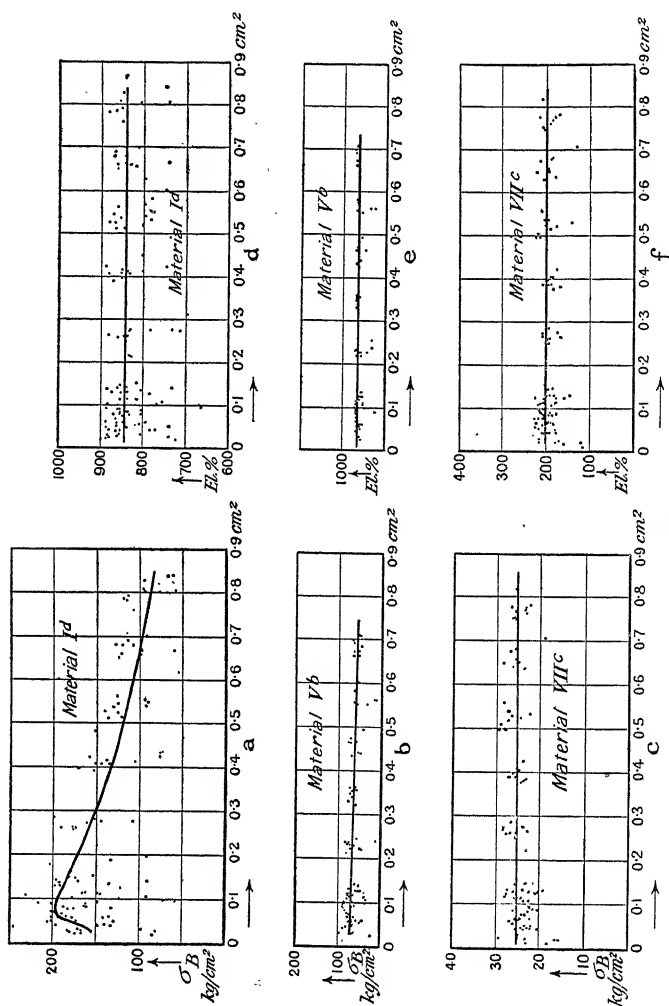


FIG. 20.

For each of the three materials in question the relation between the breaking stress ( $\sigma_B$   $\text{kg}/\text{cm}^2$ ) and the cross section ( $\text{cm}^2$ ) as shown on the left, and the relation between the elongation at break (El.%) and the cross section is shown on the right.

It will be observed again that in the case of the high-grade Material I the breaking load falls greatly with increase in the cross sectional area; that in the case of the less extensible Material V the breaking load also falls with increase in the cross section, but to a much smaller extent; and that in the case of the low-grade Material VII the breaking load is practically uninfluenced by the cross section. In all cases the elongation is approximately independent of the cross section.

The diagrams in Fig. 20 are incidentally interesting as showing the extent of the accidental variation in the breaking figures as determined by rings. Each point in the diagrams indicates the breaking-point of a single specimen. For further data regarding the accidental errors in measuring breaking figures, see pp. 342 *et seq.*

#### ROTATION OF THE PULLEYS SUPPORTING RINGS

In order that ring test pieces may show their full breaking figures, it is necessary that the pulleys round which they pass shall rotate throughout the stretching. Rings held by fixed pulleys or hooks show, owing to a crushing effect, smaller breaking figures than similar rings held by rotating pulleys.

The following table shows the results obtained in this connection by Memmler and Schob. The tests in question were made with rings 4 mm. broad  $\times$  6 mm. thick on a Schopper machine. In this machine as ordinarily employed the lower pulley is made to rotate during the stretching by means of a toothed wheel attached to the length-measuring arrangement. At the same time the upper pulley, which is loose, rotates on ball bearings. The lengths measured are the distances between the remote points of the upper and the lower pulleys. In the tests with fixed pulleys the extensions  $\alpha$  were measured between two gauge marks placed on the ring, and the extensions  $\gamma$  were referred to the inner circumference of the ring, and are comparable with the extensions measured in the case of the rotating pulleys. In Table LXXIV each figure is the mean of observations on fifteen rings.

Results recorded by Beadle and Stevens<sup>1</sup> for the breaking figures of specimens of high-grade rubber tested in the form of rings 1-1.5 mm. thick, 5 mm. external diameter and 2.5 mm. internal diameter, on a machine<sup>2</sup> in which they were stretched

<sup>1</sup> *Rubber Industry*, 1911, p. 273.

<sup>2</sup> Presumably on the machine described by Beadle and Stevens, *J. Soc. Chem. Ind.*, 1909, 28, 1111.

between hooks, may also be noticed as indicating that rings give very low figures for the breaking load when stretched between fixed supports. The best sample gave  $P_B$  only 0.58.

TABLE LXXIV

Material.	Character of supports.	$P_B$ .	$L_B$ .
I . . .	Rotating pulleys	1.177	906
	Fixed „	0.604	$\alpha$ , 803; $\gamma$ , 756
IIa . . .	Rotating pulleys	0.908	918
	Fixed „	0.215	$\alpha$ , 632; $\gamma$ , 565
Va . . .	Rotating pulleys	0.971	724
	Fixed „	0.560	$\alpha$ , 601; $\gamma$ , 560
VIIa . . .	Rotating pulleys	0.273	302
	Fixed „	0.247	$\alpha$ , 269; $\gamma$ , 242

It may be remarked that the data of Memmler and Schob indicate that, although the breaking figures with fixed supports are lower than those with rotating supports, they are not necessarily more irregular. The figures summarized in Table LXXV for individual rings of Material I may be quoted in illustration of this.

TABLE LXXV

No. of ring.	Rotating pulleys.		No. of ring.	Fixed pulleys.		
	$P_B$ .	$L_B$ .		$L_B$ .	$\alpha$ .	$L_B \gamma$ .
1	1.128	883	1	0.603	780	749
2	1.292	920	2	0.576	775	743
3	1.201	909	3	0.513	725	699
4	1.084	878	4	0.580	795	750
5	1.110	888	5	0.655	830	783
6	1.280	916	6	0.653	845	797
7	1.382	949	7	0.568	795	744
8	0.998	873	8	0.543	790	743
9	1.318	924	9	0.620	800	754
10	1.218	937	10	0.597	805	755
11	1.320	930	11	0.596	825	756
12	1.115	897	12	0.630	815	763
13	1.095	898	13	0.653	840	795
14	1.094	893	14	0.612	815	755
15	1.044	883	15	0.569	815	755
Mean .	1.177	906	Mean .	0.604	803	756

In view of this result, Beadle and Stevens<sup>1</sup> have contended that the fact of ring supports being fixed "is only of secondary importance when comparing different rubbers, the required figure being merely relative, not absolute. The conditions under which a ring is stretched when the pulley is not made to revolve, or where rounded hooks or pegs are used in place of pulleys, really accord," they contend, "more with the actual conditions under which rubber goods are subjected in every-day use." This contention would, however, seem to be hardly acceptable. For (1) admitting that a stretching test on rubber samples held by fixed grips corresponds most to actual using conditions, it is to be noted that rings give breaking figures of the same order as those obtained by using fixed grips in what may perhaps be regarded as the more straightforward tests with straight pieces only if the pulleys supporting the rings rotate; and (2) it does not appear—to judge from Memmler and Schob's data—that the figures obtained with rings over fixed pulleys bear a relation to the figures obtained with rings over rotating pulleys that is at all constant.

#### RATE OF LOADING

Mallock,<sup>2</sup> who, like other early experimenters on the stress-strain relations of rubber, added the increments of load by hand, concluded that the course of the stress-strain curve was not very seriously influenced by a change in the rate at which the load was applied. Bouasse and Carrière,<sup>3</sup> who applied the load in a continuous manner, found that the extension produced by a given load was very noticeably greater with slow loading than with rapid loading. The extensions in question in their experiments were about 500 per cent. The stress-strain curve for a slower rate of loading lay above that for a more rapid rate. The results of these authors in this connection are given more fully in Chap. XVIII.

While a more rapid rate of loading leads to a smaller elongation at a given intermediate load, and to a lower curve, than does a slower rate, it leads to a greater ultimate elongation and greater breaking load, as the following results, obtained with the Bureau

<sup>1</sup> *Rubber Industry*, 1911, p. 268.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Annales Faculté Sciences Toulouse*, 5 (2), 266.

of Standards dynamometer, show.<sup>1,2</sup> The "speed" recorded is the distance in inches by which the grips separated per minute.

TABLE LXXVI

Reference	G-18			M-1			B-1			Gy-1		
Speed .	5	25	45	5	25	45	5	25	45	5	25	45
P <sub>B</sub> (lb./in. <sup>2</sup> )	2495	2690	2720	1900	1940	1970	375	430	465	340	390	430
L <sub>B</sub> .	705	735	735	565	600	590	440	460	375	105	215	220

## INFLUENCE OF PREVIOUS STRETCHING

It has been suggested that the same test piece might be used both for a set test and for extension to the breaking-point, the latter test being carried out after the former. That this procedure is inadmissible where it is desired to study the extension curve to break will appear from Chap. XVIII. That it is also impermissible where it is only desired to obtain the breaking figures appears from tests made by Memmler and Schob.<sup>3</sup> The results of the tests in question are shown in the following table. Rings were stretched for thirty minutes under half the load which the mean of tests on ten previously unstretched rings had given as the mean breaking load of the rubber; they were then released and allowed to recover for twenty-four hours, after which period they were stretched to the breaking-point.

TABLE LXXVII

Material.		I.	II.	IV.	VI.	VII.
Previously unstretched rings (mean of 10 rings)	P <sub>B</sub>	1'243	0'155	1'026	0'201	0'200
	L <sub>B</sub>	928	274	570	134	340
Previously stretched rings (mean of 10 rings)	P <sub>B</sub>	0'827	0'141	0'646	0'184	0'191
	L <sub>B</sub>	906	254	460	130'5	345

<sup>1</sup> *Circular of the Bureau of Standards*, No. 38, 3rd edit., 1915.

<sup>2</sup> While the generalization made in this sentence holds good so far as available data go, it may be stated that a closer and more exhaustive study simultaneously of the influence of the rate of loading on the stress-strain curve and on the breaking figures with particular reference to high-grade rubber tested on the Schopper machine is to be desired.

<sup>3</sup> *Mitt. Prüfungsamt*, 1909, 27, 173.

In the case of the low-grade Materials, II, VI, VII, the effect on the breaking figures of the previous extension is only slight, but in the case of the Materials I and IV it is very great—indeed, so unexpectedly great that a confirmation of the result with other high-grade specimens would be desirable.<sup>1</sup> Experiments with straight test pieces gave a similar result for Material IV.<sup>2</sup>

The Bureau of Standards compared the effect on the breaking figures of taking to the break in the usual way, with continuous loading, and of taking to the break with a series of increasing stretches, to 100 per cent., 200, 300 and so on in succession. It was found that the repeated stretchings gave higher figures, particularly in regard to length at break, than did the single stretching. The influence of the previous stretching was greater in the case of the more extensible rubber than in the case of the less extensible. The most extensible rubber (No. 2, Table LXXI) gave for  $P_B \times L_B$  2470 lb./in.<sup>2</sup>  $\times$  740 with a single stretch and 2610  $\times$  865 with a repeated stretch; the least extensible rubber (No. 6) gave 930  $\times$  475 and 920  $\times$  565 respectively.

#### INFLUENCE OF TEMPERATURE

An investigation by Wormeley<sup>3</sup> shows that the breaking figures may be noticeably influenced by changes in the room temperature at which the tensile tests are made.<sup>4</sup> Determinations of breaking figures were made with dumb-bell test pieces at room temperatures ranging from 48–95° F. It was found that a higher temperature led to a lower breaking stress and a greater breaking length. The effect of variation of temperature was more marked at lower points of this range than at higher ones. The following figure shows the results obtained at 50, 70 and 90° F. with the five rubbers included in Table LXXI.

This figure also shows the effect of temperature on the amount

<sup>1</sup> Cf. data given by Wormeley, *Rubber Industry*, 1914, p. 255. Here samples previously stretched for one minute for the determination of set appear to give, not lower, but somewhat higher breaking figures than corresponding samples not previously stretched.

<sup>2</sup> The tests made with straight test pieces on Material I have to be left out of account owing to the fact that the material invariably broke (as already stated, p. 262) in the grips.

<sup>3</sup> *Rubber Industry*, 1914, p. 246.

<sup>4</sup> For data concerning the influence of the temperature at which the samples are held *prior* to testing, not the temperature at which the testing itself is conducted, on the position of the stress-strain curve for samples of rubber (rubber 90 : sulphur 10) in different states of cure, see Stevens, *J. Soc. Chem. Ind.*, 1918, **37**, 280T.

of set observed after extending the specimens by 350, 350, 300, 300, 250 per cent. respectively, and allowing a rest of one minute

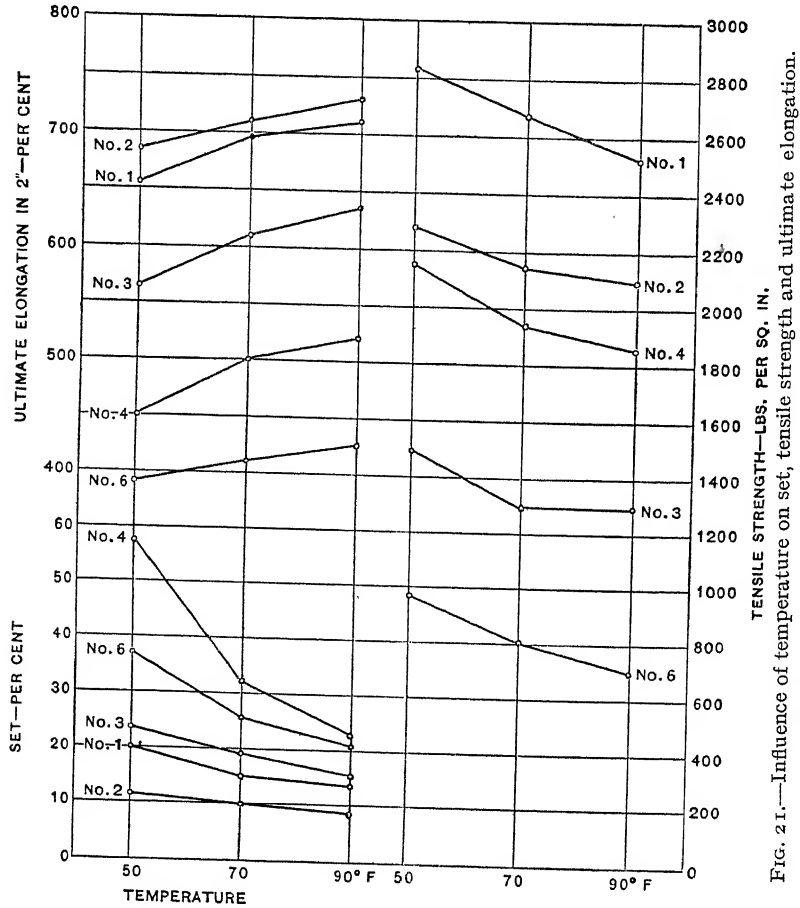


FIG. 21.—Influence of temperature on set, tensile strength and ultimate elongation.

after release. It will be observed that increase of temperature reduces the set. Cf. section in Chap. XIX on the influence of temperature on elastic after-effect.



## CHAPTER XII

### TECHNIQUE OF VULCANIZATION TESTING

*The evaluation of raw rubber.*—For the purpose of arriving at a judgment on the quality of a given sample of raw rubber, various methods present themselves for consideration. They may be distinguished as follows :—

A. Tests on the rubber in its raw state—

1. Chemical analysis.
2. Tensile tests.
3. Viscosity determinations.

B. Vulcanization of the rubber followed by subjection to—

1. Mechanical tests.
2. Chemical tests.

Now, rubber is so seldom employed technically in its raw state, that any tests made for the purpose of determining its quality must have reference ultimately to its behaviour on vulcanization. Hence, tests on the rubber in its raw, unvulcanized state will, finally, be of value for the purpose of evaluation only in so far as they can be correlated with the behaviour of the rubber on vulcanization. Further, vulcanized rubber is in most connections technically valuable because of its mechanical properties. Hence, speaking broadly, the mechanical behaviour of the rubber after vulcanization must be the final criterion for the purpose of evaluation. Chemical analysis, not only in the case of raw rubber, but also in the case of vulcanized rubber will, finally, be of value only in so far as it can be correlated with the mechanical behaviour of the vulcanized rubber.

It may be said at once that the tendency of most recent work on the evaluation of raw rubber has been in the direction of emphasizing the importance of mechanical tests on the vulcanized product. The place which chemical analysis of the vulcanized product—particularly the determination of the coefficient of

vulcanization—should occupy in the evaluation of raw rubber is now the subject of some discussion. This discussion will be considered rather fully in Chap. XIV.

The relation between the analytical quantities—ash, resin, protein, etc.—determined on the raw rubber, and the behaviour of the rubber on vulcanization, have been considered at various points in the course of Part I of this volume. It will be sufficiently clear that, although, in regard to the evaluation of raw rubber for the purpose of its technical employment, analytical determinations may be of value in certain connections, they are, generally, quite inadequate for judging the quality of rubber.<sup>1</sup>

Until somewhat recently, comparatively few chemists were employed in the rubber industry. Such chemists as were employed were largely engaged in the analytical control of the ingredients of the mixes. And when the production of plantation rubber began there was at first a disposition to regard the question of the evaluation of the raw rubber as simply a question of its analysis. But it soon became clear that judgments on the quality of samples of plantation rubber called for vulcanization tests and the mechanical examination of the vulcanized product. During more recent years—say, during the last decade—the rubber industry has begun to receive more scientific attention than it had before. And during this period the exact mechanical testing of vulcanized rubber has been introduced and to a fair extent has been developed. Prior to this period, the mechanical examination of vulcanized rubber was for the most part confined to hand and tooth tests in the factory.

In the early days of plantation production it was thought possible that, in addition to chemical analysis, mechanical tests on the raw rubber would be of value for evaluation purposes. Rubber brokers placed great emphasis on the tensile properties—the “nerve”—of raw plantation rubber as shown by hand-pulling tests.<sup>2</sup> Systematic vulcanization tests soon showed

<sup>1</sup> It may be remarked that attention is here confined practically to the clean, plantation (*Hevea*) rubbers—now the dominant class of raw rubbers. Analysis of raw rubber is of greater importance in the case of the wild rubbers, containing large proportions of resin, which formerly constituted a much more considerable proportion of the raw material used in the manufacture of rubber goods than they do to-day.

<sup>2</sup> *Valuation of raw rubber for selling purposes.*—The relative prices of batches of raw rubber is still largely decided by characters that, from the point of view of the behaviour of the rubber on vulcanization, are unimportant—particularly by the prettiness of the rubber's appearance. We are not yet within sight of a scientific system of valuing rubber for selling purposes. It may be admitted that the adoption of a hastily devised

that the tensile properties of the raw rubber were no guide to its vulcanizing properties.

#### TENSILE TESTS ON RAW RUBBER

The experience of the present writer, in tests made in 1911, was clearly to the effect that the tensile properties of raw rubber samples are not a reliable guide to vulcanizing properties. All subsequent experience has confirmed the lack of useful relation between the tensile properties of raw rubber and vulcanizing properties. It has been found that, by modifications of the procedure followed, samples of sheet can be prepared from the same batch of latex, which in their raw state differ widely in tensile properties, but which show almost identical results on vulcanization. For example: the addition of sodium bisulphite to latex may lead to the production of a more "nervous" sheet than would be produced in its absence, yet the sheet will give similar vulcanization results to a control sheet prepared without bisulphite.

It was observed, also, that the breaking figures for different portions of the same sample—say, different test pieces cut from the same smooth sheet—differed very considerably from portion to portion. This fact alone, together with the circumstance that only a comparatively small proportion of plantation rubber is prepared in a form, viz. smooth sheet, suitable for the conduct of tensile tests, is sufficient to indicate the unfeasibility of tensile tests on raw rubber as a useful means of judging quality.

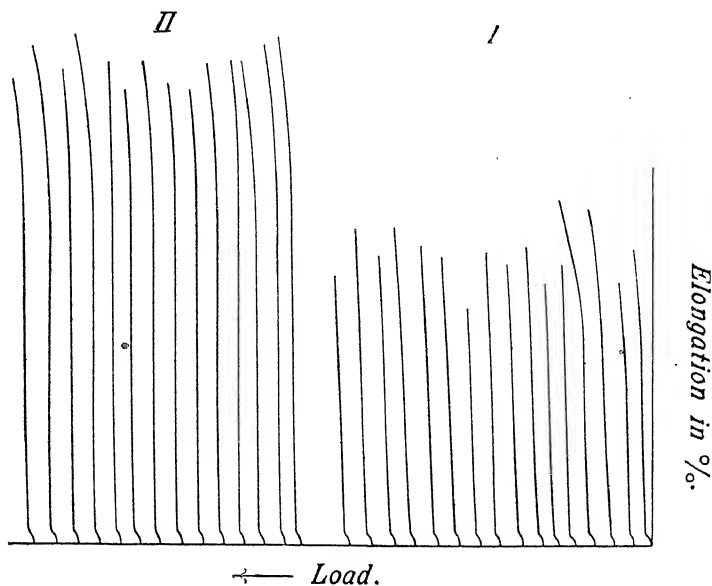
Van Heurn<sup>1</sup> has recorded the results of some tensile tests on raw rubber. He cut rings from sheets and tested them on the Schopper machine. In all cases he found very considerable variations in the breaking figures among the rings in any one batch. Thus, the figures for the sixteen samples (I), the extension

---

system of scientific valuation would be a mistake, and that the development of a system of valuation should have constant reference to the actual employment of the rubber, in technical mixes, in rubber factories, and that it requires the sincere co-operation of growers and manufacturers. Yet a system of valuing truly the raw material is so desirable from the point of view of the technical soundness of the industry, that it is greatly to be hoped that representative bodies of manufacturers and growers will combine to assist the development of a scientific system of valuation. The problem would seem to call for the appointment, for several years if necessary, of a staff of investigators, situated in part in the tropics and in part in Europe and America, working in association with a committee consisting of growers, manufacturers, plantation chemists and works chemists.

<sup>1</sup> *Meded. Delft*, 1916, pp. 442, 357; *Delft Communics.*, p. 98.

curves of which are shown in the following figure, ranged from  $0.181 \times 616$  to  $0.081 \times 423$  for  $P_b \times L_b$ .



I. Untreated Hevea sheet.

II. Same rubber, swollen in benzene and then dried.

FIG. 22.—Stress-strain diagrams for samples of raw rubber (drawn on the Schopper machine).

It will be observed from the above figure that in the stress-strain curve for raw rubber the feature which is characteristic of the stress-strain curve of high-grade vulcanized rubber, viz. contrasted steep and flat portions, is not discernible.

The samples II included in the above figure represent samples obtained after swelling<sup>1</sup> the sheet from which samples I were taken in benzene and allowing the latter to evaporate. The effect of this treatment was greatly to increase the extensibility of the raw rubber; the average breaking length being increased from 527 to 864 per cent. (The breaking load increases only from 0.104–0.121).

Van Heurn found samples taken from the middle portion of a sheet to be stronger than samples taken round the outside; the

<sup>1</sup> For an earlier and extensive study of the swelling of raw rubber in organic liquids, see Posnjak, *Koll.-Chem. Beihefte*, 1912, 3, 417.

mean breaking figures of seven samples from the middle being  $0.16 \times 571$  and of seven samples from the side  $0.20 \times 580$ .

The same observer compared, for a number of samples of raw rubber, the breaking figures with the viscosity of the rubber, (a) in its original state, (b) after heating for several hours in carbon dioxide at temperatures ranging from  $100-140^\circ$ , and (c) after breaking down on the mixing rolls. He found for rubber which had been subjected to such treatments a direct proportionality between the breaking stress and the viscosity number. The following table shows the results for one sheet.

TABLE LXXVIII

	Viscosity No.	P <sub>B</sub> .	L <sub>B</sub> .
Original sheet . . . . .	63.6	0.11 (mean of 9 rings)	537 (mean of 9)
After heating for $5\frac{1}{2}$ hrs. in carbon dioxide at $100^\circ$	51.8	0.09 (mean of 7)	506 (mean of 7)
After breaking down on the mix- ing rolls	11.7	0.0215 (mean of 6)	485 (mean of 4)

It is not to be concluded, from the proportionality found under such circumstances between the tensile results for raw rubber, and the viscosity of its solutions, that the tensile strength of raw rubber forms an index to its vulcanizing quality. It would hardly be maintained, for example, that the three samples included in the above table would yield seriously different results on vulcanization, despite their differences in regard to viscosity and tensile strength, or that samples II, Fig. 22, would give vulcanization results appreciably different from those given by samples I shown in the same figure. The very limited extent to which viscosity is an index to vulcanizing properties is pointed out in Chap. XVII. And even if the viscosity were a satisfactory index to vulcanizing quality, there is no evidence that in general the breaking figures of different samples of raw rubber are proportional to their viscosities. The investigation mentioned above dealt only with the effect of different treatments—heating and “breaking down”—on given samples of rubber, and did not compare different samples in their original condition.

It is suggested by the Delft Institute,<sup>1</sup> that, where rubber is to be used in its raw state, its value, particularly in regard to its adhesive properties, may be indicated by its tensile strength.

#### TECHNIQUE OF EXPERIMENTAL VULCANIZATION

*Outline of vulcanization operations.*—The so-called vulcanization<sup>2</sup> of rubber gives to rubber mechanical and physico-chemical properties, which in its raw state it does not possess, or possesses only in a smaller degree, and which make its possible technical applications vastly greater in number and importance in its vulcanized than in its raw condition.<sup>3</sup> High-grade vulcanized rubber is more extensible, will withstand greater stresses, recovers more readily from deformation than raw rubber; it is insoluble in the organic solvents which will dissolve crude rubber; it is less susceptible than raw rubber to the influence of heat, cold, sunlight and chemicals.

Vulcanization depends essentially upon treatment of the raw rubber with sulphur.<sup>4</sup> Vulcanization may be brought about in (1) the cold way, (2) the hot way. The former method has only a limited application. It can be used only where thin layers of rubber are in question, as in waterproof fabric, bathing caps,

<sup>1</sup> *Delft Communic.*, p. 101.

<sup>2</sup> The term vulcanization was proposed by Mr. Brockendon, a colleague of Hancock's in the firm of Chas. MacIntosh & Co. See the very interesting volume, *Personal Narrative of the Origin and Progress of the Caoutchouc or India-Rubber Manufacture in England*, by Thomas Hancock, London, 1857.

The process of vulcanization was first discovered by Goodyear in 1839. Three years later it was discovered independently by Hancock. It appears from Hancock's *Personal Narrative*, that, from an external examination of a sample of vulcanized rubber which Goodyear had sent by an agent to Hancock's firm, it was at once recognized that the material contained sulphur. It appears that, starting from this clue, Hancock advanced to an independent discovery of vulcanization. This historical point has been discussed clearly by Porritt in a lecture before the Royal Society of Arts, "The Rubber Industry—Past and Present," reprinted *I.R.J.*, 1919, pp. 441, 445, 489.

<sup>3</sup> L'esprit étonné se demande, non pas à quoi on emploie le caoutchouc, mais bien à quoi cette substance n'a pas été encore utilisée,"—Aimé Girard (quoted in *Le Caoutchouc, sa Chimie nouvelle*, A. Dubosc and A. Luttringer).

<sup>4</sup> Boggs (*J. Ind. Eng. Chem.*, 1918, 10, 117) has shown that selenium is capable of bringing about vulcanization with limited success. Ostromislenski (*J. Russ. Phys. Chem. Soc.*, 1915, 47, 1462, 1467, 1885, 1898, 1904) has claimed that vulcanization can be brought about by a variety of other agents, such as aromatic nitro-compounds and organic peroxides. Tests made by Stevens and Bunschoten afford a limited confirmation of Ostromislenski's claims. The field which Ostromislenski's discoveries open awaits a wider exploration.

etc. The vulcanizing agent employed is sulphur chloride,  $S_2Cl_2$ . This is applied in a dilute (say, 2 per cent.) solution in a rubber solvent. The latter swells the rubber and so creates conditions suitable for the action of the vulcanizing agent. The period of exposure of the rubber to the action of the vulcanizing solution is very brief. Cold vulcanization has been studied to a certain extent in relation to the theory of vulcanization,<sup>1</sup> but in its relation to the mechanical properties of the product produced by its use has been studied hardly at all.<sup>2</sup>

Apart from the fact that in practice the vulcanization of the great majority of rubber goods is not done in the cold way, this method of vulcanization has not commended itself as a convenient one for the experimental study of the vulcanizing properties of rubber. In the experimental study of the vulcanizing properties of rubber, the hot way of vulcanizing has been employed practically exclusively. In the hot way the rubber is put through the following operations: It is first rendered plastic by working it between hot steel rolls (the mixing rolls) running in opposite directions at unequal speeds. The mixing rolls are provided internally with both steam pipes and cold-water pipes, so that their temperature can be regulated.

When, as a result of the joint effect of the heat and the milling, the rubber is sufficiently plastic, sufficiently "broken down," the vulcanizing agent—sulphur in a state of fine powder—and, for most technical purposes, other materials ("fillers") are incorporated ("compounded"). The resulting "dough" or "stock" is then—in factory practice, usually after a period of rest—converted, for the greater number of technical purposes and invariably for experimental vulcanization work such as that discussed in the present volume, into smooth sheets of definite thickness. The rolling machine employed for this conversion is known as a calender, and consists of three internally heated steel rolls lying vertically one above the other. Adjoining rolls rotate in opposite directions. The dough is fed in between the

<sup>1</sup> Cf. Hinrichsen, *Chem.-Ztg.*, 1893, **17**, 634; 1894, **18**, 701, 1155; *Koll. Zeit.*, 1911, **8**, 250; Hinrichsen and Meisenburg, *Chem.-Ztg.*, 1909, **33**, 735, 756; Hinrichsen and Kindscher, *Koll. Zeit.*, 1910, **6**, 202, **7**, 65; Bysow, *ibid.*, 1910, **6**, 280, **7**, 160; Bernstein, *ibid.*, 1912, **11**, 185.

<sup>2</sup> Van Heurn (*Meded. Delft*, 1916, p. 429; *Delft Communics.*, p. 221) has made a few observations on the effect of increasing periods of cold curing on the breaking-point. He found the latter, for strips 0.2–0.25 mm. thick, immersed in a 2 per cent. solution of sulphur chloride in carbon bisulphide, to increase up to a period of immersion of 1–2 minutes, and then to remain practically unchanged on further increase of the period of immersion.

two upper rolls; it emerges on to the middle roll as a smooth sheet and is carried round by the middle roll until it meets the lower roll. Between the two lower rolls calico passes from a reel on one side of the machine to a reel on the other. The smooth sheet of dough, known as calendered sheet, is carried away on the calico and wound up with the latter on the second reel. The calico prevents the layers of calendered sheet from sticking together. For experimental purposes the distance between the rolls of the calender is adjusted so that the resulting sheet is quite thin—1 to 2 mm. Suitable slabs for experimental purposes may be built up from several thicknesses of such thin calendered sheet.<sup>1</sup>

For tensile tests with rings, on the Schopper machine, a thickness of 5 mm. in the vulcanizate has been employed by most workers.<sup>2</sup> For tensile tests with dumb-bell test pieces, on a Bureau of Standards or a Scott machine, a thickness of  $\frac{3}{32}$  in. (approximately 2.5 mm.) is perhaps most usual.<sup>3</sup> In making up slabs from calendered sheet, the layers of the latter should be rolled together (with a hand roller) criss-cross, so as to neutralize any possible influence of "grain" (cf. p. 265).

Vulcanization of the compounded rubber is brought about by the action of heat.<sup>4</sup> In the manufacture of rubber goods the manner of applying the heat differs according to the character of the rubber compound and of the goods which are in process of manufacture. In some cases the material is exposed directly to steam in an autoclave or of air in a hot-air chamber, but perhaps most generally the rubber is under pressure during vulcanization; it is commonly contained in a mould, which in many cases is pressed between steam-heated plattens.

<sup>1</sup> The question as to how far specially prepared slabs are adequate for testing rubber in relation to its use for the manufacture of particular kinds of rubber goods cannot be discussed here. For the purpose of testing of the general character with which the present volume is concerned, the specially prepared slab is clearly called for.

<sup>2</sup> Schidrowitz and also Whitby (*J. Soc. Chem. Ind.*, 1916, **35**, 493) have used a thickness of 3 mm. The objection to the ring-shaped test piece that such a test piece does not give the full breaking figures, has less force, the smaller the cross section of the ring.

<sup>3</sup> Using dumb-bell test pieces twice the thickness mentioned here (and  $\frac{1}{2}$  in. wide), the present writer found the breaking figures to be considerably lower than would have been expected with thinner pieces (cf. p. 273).

<sup>4</sup> In factory practice the temperature of vulcanization is usually expressed in terms of steam pressure. The following table shows pressures and corresponding temperatures:—

Steam pressure (lb./in. <sup>2</sup> )	25	30	35	40	45	50	55
Temperature (°C.)	130.1	134.4	138.1	141.4	144.6	147.5	150.2



In experimental work, such as that dealt with in the present volume, the rubber is generally enclosed in a simple form of mould during vulcanization. The methods of applying the heat are considered later.

In general, it may be said that the pieces of apparatus used in the preparation of rubber for experimental work are, substantially, small-scale copies of the plant actually employed in rubber factories.

*Preliminary washing.*—In the case of wild rubbers, such as those exclusively employed in the rubber industry prior to the advent of the plantation product, it is necessary, owing to the presence of impurities or to a high water-content and an unsuitable form, that, as a preliminary step to compounding, the rubber shall be washed and dried. For this purpose the rubber is crêped on mills similar to but in factory practice larger than those used for crêping the wet coagulum on the plantation. When plantation rubber first came into use in rubber manufacture, the rubber factories at first submitted it to a preliminary washing and crêping such as that employed in the case of wild rubber. But it is now generally accepted that for the most part <sup>1</sup> plantation rubber is produced in a form sufficiently clean and dry to allow of its being compounded at once; and it is no longer the custom generally to wash plantation rubber at the rubber factory.

While it is usually unnecessary to wash the ordinary plantation forms of sheet and crêpe, it may be necessary, where plantation rubber is in a massive form, such as "slab," to convert it into crêpe before compounding. On this account, and on account of the fact that it is still considered necessary in occasional cases to wash the ordinary forms of plantation rubber, the question of the possible effect on the vulcanization results of such preliminary washing and crêping should be considered briefly.

*Influence of washing dry rubber on vulcanizing properties.*—It appears that such preliminary washing is, generally,<sup>2</sup> not likely to influence the vulcanization results. Of a number of experi-

<sup>1</sup> See, however, discussion, p. 165, on the washing of plantation lower grades.

<sup>2</sup> The possibility of washing and crêping removing a certain amount of the accelerator or accelerators from rapid-curing rubbers, such as matured rubbers, particularly if the washing is very thorough and the rubber is rolled out very thin, should be mentioned. The Delft Institute state (*Delft Communics.*, 182) that they have found such a removal of accelerators and a consequent reduction in the rate of cure in the case of Fine Hard Para, but they have not published any numerical data on the subject.

ments bearing on this point, the following may be quoted.<sup>1</sup> A mass of rubber prepared in the style of Fine Hard Para was divided into two portions; one portion (A) was crêped in a rubber factory according to the usual procedure of the factory and was allowed to dry; from the other portion (B) a dry product was obtained merely by cutting into pieces and drying in a vacuum desiccator. Vulcanization tests (in the mix rubber 100: sulphur 8, cured at 141°) were then applied. The crêped and the uncrêped samples gave substantially identical results, as is shown in the following table:—

TABLE LXXIX

	Time of cure.	Slope.	P <sub>B</sub> (lb./in. <sup>2</sup> ).	L <sub>B</sub> .
A (crêped) . . .	2½ hrs.	38	2137	1019
B (uncrêped) . . .	2½ hrs.	38	2125	1017

Eaton<sup>2</sup> has also reported experiments from which he comes to the same conclusion as that stated above. He examined eight samples of unsmoked and ten samples of smoked sheet in their original condition and after crêping on washing mills. In no case was the rate of cure or the breaking stress affected by the crêping.

*Mixing.*—The compounding operations are of such a nature—involving, as they do, a rather considerable element of individual judgment in adjusting the temperature of the mixing rolls, in deciding as to the amount of “breaking down” called for before the compounding ingredients are added, in deciding as to the amount of working necessary, after the addition of the compounding ingredients, in order to secure a homogeneous mix, and in a number of other particulars—that the question as to how far uniformity is or can be secured in the mixing operations, and as to how far deviations from a uniform procedure may influence the vulcanized product, suggests itself for consideration in connection with the technique of experimental vulcanization work.

Automatic mixers have been devised, but have not hitherto found extensive employment. They would, however, appear to represent a step in the right direction. An interesting sugges-

<sup>1</sup> Whitby, *Jour. Soc. Chem. Ind.*, 1916, 35, 493.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 305.

tion is to measure the degree of plasticity of the dough by noting the electrical power consumed over a time interval in an electrically driven automatic mixer.<sup>1</sup>

When, with the recent development of scientific interest in the rubber industry, experimental vulcanization tests began to be undertaken, it was suggested in some quarters that the element of individual judgment in the compounding operations was so considerable, and its influence on the quality of the vulcanized product so important, that satisfactory mixes could be made only after years of experience, such as that possessed by a foreman mixer in a rubber factory. Such, however, is not the case. Undoubtedly a certain amount of experience is necessary in order to perform satisfactory and consistent mixing, but the scientific worker, or, in fact, any person of ordinary intelligence, can secure such experience in a comparatively brief time—at all events where plantation rubber and simple mixes, such as those with which published investigations mostly deal, are concerned.<sup>2</sup>

Eaton,<sup>3</sup> who works in the Malay States, quotes some interesting data, showing the constancy of mixings made by trained native assistants. Eight separate mixes (rubber 90 : sulphur 10) were made with each of two rubbers—a rapid- and a slow-curing one. A comparison of the breaking figures and of the stress-strain curves for the different mixes at a number of different periods of cure showed variations very little greater than those which would have been obtained for a number of different test pieces from a single mix.

Van Heurn<sup>4</sup> prepared four separate mixes of 255 g. raw rubber and 45 g. of a mixture of sulphur, lead oxide, and magnesia (7.5 : 5 : 2.5 parts), and vulcanized the mixes separately for 10 minutes in steam at 52 lb. (148°). From each vulcanizate 8 or 9 ring test pieces were tested. The average of the results for each vulcanizate is shown in Table LXXX. The fluctuations in the results here seen represent not the results of variation in the mixing only, but the sum-total of variations

<sup>1</sup> Grundy and Schidrowitz, "Apparatus and Method of Measuring Plasticity of Rubber and Rubber Mixings," *Eng. Pat.* 15,438 (1915).

<sup>2</sup> Admittedly the satisfactory handling of low-grade, resinous, wild rubbers and of certain compounding ingredients is more difficult. Such materials, however, are not in question in the work with which the present volume deals.

The possibility of difficulties due to pre-vulcanization on the rolls in making mixes containing accelerators should be mentioned. They can usually be avoided.

<sup>3</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 38.

<sup>4</sup> *Delft Communics.*, p. 161.

in the mixing, calendering, vulcanizing and tensile testing. It will be seen that the fluctuations are not very large.

TABLE LXXX

No. of mix	1	2	3	4
P <sub>B</sub>	1.13	1.22	1.20	1.21
L <sub>B</sub>	768	780	789	778

*Influence of working on properties after vulcanization.*—Regarding the effect on the vulcanizing properties of exceptionally severe treatment on the mixing rolls, the following conclusions appear to be established: (1) The rate of cure is unaffected. (2) The course of the stress-strain curve is unaffected.<sup>1</sup> (3) The breaking figures are affected adversely, *i. e.* the stress-strain curve ends at an earlier point in its course.

C. O. Weber,<sup>2</sup> Alexrod,<sup>3</sup> and Spence and Ward,<sup>4</sup> all concluded that extra working on the mixing rolls diminishes the breaking stress and the elongation at break. Alexrod found that rubber which had been "broken down" to an excessive extent showed a higher vulcanization coefficient than rubber which had been subjected only to the normal amount of working. He saw in this conclusion a main support for his view of the nature of the vulcanization process, as involving a preliminary disaggregation of the caoutchouc units. His conclusion must, however, be regarded as incorrect. Weber and also Spence and Ward agreed in finding the rate of combination of sulphur to be unaffected by extra milling; and are confirmed by experiments more recently conducted by Dekker.<sup>5</sup>

Spence and Ward made two mixes, rubber 100 : sulphur 10, from a given sample of Fine Hard Para. In preparing Mix I, the rubber was "worked" on moderately hot rolls for 30 minutes, the sulphur was then added, and 10 minutes further working was given for the purpose of mixing. In preparing Mix II, a similar procedure was followed, except that the working prior to the introduction of sulphur lasted 90 minutes. Slabs 4 mm. thick were vulcanized at 135° for periods of from 1–8 hours. Ring test pieces were cut for examination on the Schopper

<sup>1</sup> *Delft Communics.*, p. 205. The data in substantiation of this conclusion have not yet been published. It is further concluded by the Delft Institute that on *very* prolonged working the rate of cure and the course of the stress-strain curve may be altered.

<sup>2</sup> *The Chemistry of India-Rubber*, London, 1906, p. 16.

<sup>3</sup> *Gummi-Ztg.*, 1909, **24**, 352.

<sup>4</sup> *Koll. Zeit.*, 1912, **11**, 278.

<sup>5</sup> *Delft Communics.*, p. 181.

machine. The breaking figures, shown in the following table, are the mean of several independent tests:—

TABLE LXXXI

Period of vulcanization (hrs.)	1	2	3	4	5	6	7	8
Mix I { $P_B$ (lb./in. <sup>2</sup> )	242	639	890	1510	1750	1783	244	234
{ $L_B$ . . . . .	1008	978	973	932	912	855	376	324
{ Combined S (%) .	1.03	1.62	2.25	3.16	3.90	4.28	5.40	5.83
Mix II { $P_B$ (lb./in. <sup>2</sup> )	224	557	805	1381	1577	1632	1716	471
{ $L_B$ . . . . .	985	949	906	935	901	845	804	572
{ Combined S (%) .	0.84	1.59	2.45	3.30	3.83	4.34	5.16	5.75

A further and more exact series of small-scale vulcanizations, unaccompanied by tensile tests, for periods up to 20 hours was conducted, and served to confirm the identity of the vulcanization coefficients in the two mixes at the same curing period.

Recent tests by van Heurn<sup>1</sup> confirmed conclusion (3), viz. that extra working reduces the breaking figures. One half of a sample of rubber was worked on the rolls for 10 minutes before being mixed with 7.5 per cent. of sulphur, 5 per cent. of litharge, and 2.5 per cent. of magnesia; the other half was worked for 30 minutes before being similarly mixed. Vulcanization was brought about by 10 minutes' heating at 50 lb. steam pressure. The results of tensile tests on the vulcanizates are shown below:—

TABLE LXXXII

Period of working	10 mins. (Mean of 9 rings)	30 mins. (Mean of 5 rings)
$P_B$ . . . . .	1.27	1.11
$L_B$ . . . . .	758	764

In the above tests the working was deliberately continued far beyond the point to which it would be carried normally in making a mix. It was concluded that any differences, produced in the tensile results by variations, such as may occur under normal conditions of mixing, will be within the normal limits of irregularity for breaking figures.

#### METHODS OF VULCANIZATION

For the purpose of vulcanizing sheets from which test pieces are to be cut for experimental work, while considerations of convenience and rapidity in handling the form of apparatus

<sup>1</sup> *Meded. Delft* 1916, p. 376.

chosen are not to be neglected, the most important consideration is probably the degree of exactness with which the temperature can be controlled. The importance of exact control of the temperature can readily be appreciated when it is remarked that an increase in temperature of  $10^{\circ}$  nearly trebles the speed of vulcanization.

*The steam press.*—So far as convenience and rapidity of handling are concerned, the hydraulic steam press commends itself, and is, in fact, very generally used for routine testing work in rubber factories. The press consists of a number of flat, hollow plattens, heated internally by steam. Between the plattens sheets of calendered rubber or rubber in flat moulds can be subjected to pressure and heat simultaneously. The upper and lower parts of the mould used are fitted together without bolts and screws; and this gives the steam press a very marked advantage in regard to rapidity of handling over other forms of vulcanizing apparatus, in which the mould is closed by screws. Also, the press is more rapid than the autoclave because no time is consumed in blowing off steam at the conclusion of a cure. Despite its convenience, however, the steam press has not generally commended itself for experimental work aiming at the greatest feasible exactness, chiefly because of the difficulty of controlling the temperature with sufficient nicety—at all events in the small-scale, laboratory plants.<sup>1</sup> And vulcanization in an autoclave has been most generally adopted for research work.<sup>2</sup>

*The autoclave.*—The rubber may be wound round with calico, but is usually contained in a mould; and the latter is placed directly in the steam. The autoclave is advisably steam-jacketed. (An autoclave arranged for indirect steam heating, *i. e.* having steam fed only into a jacket, is not recommendable, owing to the unsatisfactory conduction of heat by air. "Live" steam is called for.) The autoclave or vulcanizing pan is conveniently of a shallow construction and stands on three short legs. The cover is closed by bolts and screws, and has a balance weight attached for convenience of opening and closing. The autoclave should be large enough to take a fair number of moulds. It is

<sup>1</sup> For experiments on extremely rapid stocks, such as those curing in a few minutes, which it is possible to produce by the use of artificial accelerators, the steam press would seem to have advantages, as it is necessary in such cases that the period of heating shall be sharply defined, *i. e.* that the rubber shall be removed without delay from the hot mould.

<sup>2</sup> Vulcanization in electrically heated moulds has been proposed (*e. g.* *Fr. Pat.* 345,605 of 1904. Cf. also *Le Caoutchouc*, 1918, 15, 9576; *I.R.J.*, 1918, 56, 561), but has not hitherto been tried for testing work.

well to have the temperature shown both by a steam gauge and by a thermometer. The latter is placed in a well, containing a little mercury, sunk in the cover.

The moulds used to contain the rubber during vulcanization in an autoclave are of simple construction. If it is desired to vulcanize discs, one of which will serve for one test ring, a simple screw mould, in which the head screws on to the rubber contained in the lower part of the mould, may be used. It is better, however, to prepare, instead of discs, rectangular slabs of a size which will permit of more than one test piece being cut from each slab. For the purpose of holding such rectangular slabs, the mould described by Eaton<sup>1</sup> is convenient. It consists of a rectangular frame, exactly 5 mm. in thickness, divided by cross pieces into four compartments, each of which measures  $126 \times 61$  mm. and holds a slab from which two Schopper rings can be cut. A short portion is cut away from each compartment of the frame, in order to allow excess of rubber to spew out during vulcanization. The frame is screwed between steel plates  $12 \times 9 \times \frac{3}{4}$  in., with smooth inner surfaces. The plates are provided with handles.

From the calendered sheet, which has been made up to a thickness of slightly more than 5 mm., portions, weighing 40 g., and slightly smaller in area than the size of one compartment, are cut. The sides of the slab are dusted with French chalk.<sup>2</sup> Tracing cloth or other suitable material is interposed between the rubber and the outside plates of the mould, in order to obviate irregularities ("lakes") in the surface of the vulcanizate. It is possible to prepare test pieces with a maximum variation in thickness of  $\pm 2$  per cent., *i. e.* from 4.9 to 5.1 mm. In view of what was said in the preceding chapter on the influence of the cross section of the test piece on the tensile results, the importance of uniformity in the thickness of the test piece where exact comparative results are desired will be appreciated.

For the purpose of measuring the thickness of the rubber test slabs, a micrometer screw gauge of the ordinary type is unsuitable, owing to the softness of the material. A special form of micrometer, provided with enlarged contact surfaces and ratchet stop—the latter making it possible to measure each sample under the same pressure—such as is employed for paper and textiles,

<sup>1</sup> *Loc. cit.*, p. 29.

<sup>2</sup> The present writer is not entirely favourable to the usual practice of dusting samples for vulcanization with French chalk, where exact results are desired, as some of the powder may become incorporated with the rubber and produce a slight but appreciable effect on the tensile results.

is used. The "automatic thickness tester" of Schopper, which shows on a large dial face the thickness to 0.01 mm., as measured under a standard pressure, is very convenient (see Plate VIII).

*The oil-bath.*—An oil-bath may be used for the purpose of vulcanization with satisfactory results. This method of vulcanization has been adopted by the Delft Institute for most of their vulcanizations and has been tested extensively by them. A large bath, filled with a petroleum product of a suitable character,<sup>1</sup> and supplied with a stirring arrangement and means for suspending the moulds, is used. Advantages which may be claimed for the oil-bath vulcanizer are as follows: (a) Moulds can be introduced or withdrawn without interfering with other samples in the vulcanizer. Hence, cures of different lengths can be carried on alongside one another, and moulds can be put in just as they are made ready. With the autoclave vulcanizer it is necessary to have all the moulds ready at the same time and to withdraw them all at the same time: (b) Its use simplifies the minimal laboratory installation required for vulcanization testing; for a boiler, providing steam, is not called for. (The heating of experimental mixing rolls and calender can be accomplished by hot water produced by a coil heater.)

Extensive trials with an oil-bath vulcanizer were conducted by van Heurn and van Rossem,<sup>2</sup> with the object of comparing results obtained in such a vulcanizer with those obtained in an autoclave, and with the further object of comparing the results obtained in the oil-bath among themselves, so as to ascertain their degree of constancy. When using an autoclave, the vulcanizing conditions employed by these workers are: 4 minutes "rise" to a temperature of 148.25° (representing a steam pressure of 52 lb. or 3.5 atmospheres), followed by 1½ hours cure at this temperature. In the case of the oil-bath vulcanizer, there is no "rise," the oil being already at the vulcanizing temperature when the moulds are introduced. Further, owing to the specific heat of oil being higher than that of steam, it was to be presumed that the rubber would reach the vulcanizing temperature more quickly in the oil-bath than in the autoclave. Hence, it was to be anticipated that, in order to obtain the same results as those

<sup>1</sup> The oil should be capable of being heated for a long period at, say, 150° without smoking. The oil employed by the Delft Institute is described as "paraffine liquidum." The present writer has found a light engine oil, known in the Standard Oil system as "Zone oil," to be sufficiently satisfactory.

<sup>2</sup> *Meded. Delft*, 1916, p. 186.



given by the above-mentioned standard conditions in the autoclave, a slightly lower temperature would be required. This was found to be the case. Trials in the oil-bath were made at 150°, 148° and 147°; and the results were compared with the results in the autoclave at 148·25°. It was concluded that for a cure of 1½ hours a temperature of 147° in the oil-bath was equivalent to a temperature of 148·25° in the autoclave. In the following table the results of the comparison of these temperatures are summarized:—

TABLE LXXXIII

<i>Autoclave</i> (2 slabs cured).		<i>Oil-bath</i> (33 discs cured).	
P <sub>B</sub> (mean of 11 rings) .	0·95	P <sub>B</sub> (mean of 33 rings) .	0·96
L <sub>B</sub> ( " " " " ) .	981	L <sub>B</sub> ( " " " " ) .	989
Vulcn. coeff. (1 detn. only) .	3·07	Vulcn. coeff. (mean of 33 detns.) .	3·10

Comparing the samples vulcanized in oil among themselves, it was concluded that the probable errors in breaking figures were smaller than those affecting tests in which the autoclave was used, and that the stress-strain diagrams for tests in which the two different vulcanization methods had been used were, except for accidental errors and differences due to variation in thickness of the test pieces, coincident.

The moulds employed by the above-mentioned workers are circular, and are designed to hold a disc suitable for a Schopper ring. The two parts of the mould fit into each other with conically ground planes. They are bolted together at four points and are provided with additional screws, the object of which is to raise the cover, for the purpose of opening the mould, without damaging the conical planes. The interior of the mould is shaped so that a trench runs round the rubber disc. In this trench a few drops of water are placed, with the object of avoiding porosity in the vulcanizate.<sup>1</sup>

<sup>1</sup> *Porosity*.—Van Iterson (*Meded. Delft*, 1916, p. 126; *Delft Communics.*, p. 223), had concluded, from his investigation of the cause of porosity in rubber, that, for the purpose of avoiding porosity in the test piece, it is necessary to maintain round the test piece during vulcanization a pressure greater than or equal to the tension of water vapour at the temperature of the rubber.

Van Iterson's investigation led him to regard porosity as arising most frequently in the following way: During the blowing off of an autoclave the temperature surrounding the rubber is liable to fall more rapidly than the temperature of the rubber itself, with the result that the small quantity of moisture which may be present in the rubber (0·2 per cent. is sufficient) may be converted into steam, and may, particularly if the rubber is con-

The present writer has employed an oil-bath vulcanizer with satisfactory results. Rectangular moulds were used; the test slabs being of a size which would give two dumb-bell test pieces. The moulds were made from two rectangular pieces of  $\frac{3}{4}$  in. boiler plate, a suitable depression being cut in one of the pieces for the reception of the test slab. It was found that the mould could be made oil-tight by placing between its two plates thin lead sheet and applying thinly a paste of litharge and glycerine.

#### CUTTING TEST PIECES

Test pieces with satisfactory outlines cannot be obtained directly by moulding, but must be cut from a vulcanized slab by means of a die or dies. In the case of dumb-bell-shaped test pieces a single cut only with a die, of appropriate shape, the edge of which is wetted, is required; the rubber being placed on a slightly yielding surface, such as that supplied by a piece of

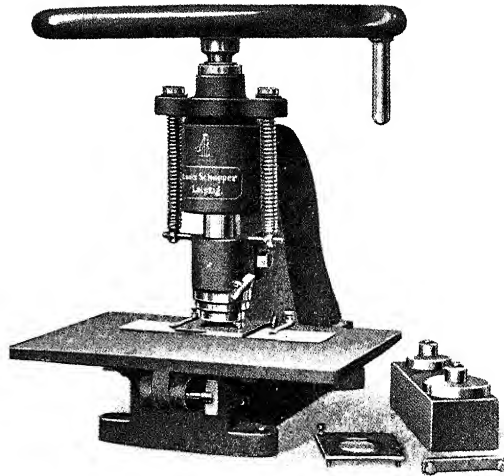
---

siderably under-vulcanized, and, hence, of low tensile strength, produce permanent pores.

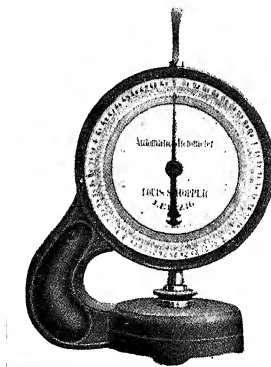
Of a number of experiments described by Van Iterson, reference may be made to the following: Three small cylinders of the same rubber-sulphur compound were put in three strong glass tubes; one tube was sealed; another was sealed after the introduction of a few drops of water; and the third was drawn out. The tubes were heated simultaneously in an oil bath at  $148^{\circ}$  for  $1\frac{1}{2}$  hours, the drawn-out end of the third tube projecting from the oil. The vulcanizate in the first tube was somewhat porous, in the second tube perfectly free from pores, in the third tube spongy and swollen. Clearly the tension in the second tube had prevented the formation of pores. The tension in the first tube—due to the air and the moisture present in the rubber—has been insufficient to prevent porosity entirely. In a further experiment it was shown that the necessary tension could be supplied (instead of by introducing water) by connecting the upper end of the tube with a mercury gauge in which the difference of levels during vulcanization was 270 cm. (corresponding to a pressure of about  $3\frac{1}{2}$  atmospheres).

The following experiment illustrates the conclusion that steam generated in the rubber during cooling may produce porosity in a soft, under-cured vulcanizate, while it is not able to produce porosity in a stronger, more fully cured vulcanizate.—A strip of calendered sheet 7 mm. thick (rubber 92.5: sulphur 7.5), clamped between glass plates, was placed in a glass tube, in the bottom of which was 10 c.c. of water. The tube was drawn out at one end and its body placed in a heated oil-bath. The water was allowed to boil away until practically all the air in the tube had been expelled. The tube was then sealed off. It was removed from the oil-bath and cooled under a jet of water. It could be observed that, as a result of the cooling, the rubber, at this stage plastic, quickly swelled up into a spongy mass. The tube was now reintroduced into the bath at  $150^{\circ}$ . It could be seen that the pores disappeared rapidly and that the rubber regained its original shape. The temperature of the bath was raised to  $161^{\circ}$  and maintained at that point for one hour. The tube was then removed and again cooled in a jet of water. The rubber, now fully vulcanized, was found to be free from porosity.

PLATE VIII.



Schopper's Ring Punching Machine for making  
Standard Test Pieces.



Schopper's "Automatic" Micrometer.

leather. Provided that the edge of the die is kept sharp, satisfactory test pieces can be obtained.

The punching of a ring of perfectly uniform width (approximately 4 mm.) presents a more difficult problem than the punching of a dumb-bell shaped test piece, as two cuts, accurately centred and vertical, are required. The cutting press and accompanying circular knives made by Schopper (see Plate VIII) solve the problem. They do beautiful work.

#### PERIOD OF REST BEFORE TESTING

Owing to the fact that the tensile properties of samples of vulcanized rubber are frequently observed to change on keeping, it is necessary to consider the question of fixing a suitable period of rest between vulcanization and testing. On the one hand it is to be desired, for the purpose of securing uniform conditions of comparison, that the period of rest shall be sufficiently long to allow the rubber to arrive at a position as nearly stable as possible; and on the other hand it is to be desired, for the purpose of obtaining an evaluation of the rubber in the shortest time feasible, that the period of rest shall be as short as is consistent with the former desideratum.

The most usual period of rest employed in the published work has been three days. A recent investigation by de Vries and Spoon,<sup>1</sup> however, shows that a period of rest of 24 hours is sufficient.<sup>2</sup> A collection of 26 samples, comprising different types of plantation rubber, was examined. In the case of each sample, after mixing 92.5 parts of rubber with 7.5 parts of sulphur, five slabs, each sufficient for 6 Schopper rings, were vulcanized together at 148°;<sup>3</sup> and rings cut from the slabs were subjected to tensile tests 24, 48, 72, 96 and 120 hours, respectively, after vulcanization. The tensile results for each slab were thus the mean of tests on 6 rings. Excluding 4 exceptional specimens, the results for tensile strength,  $L_B$ , may be summarized as follows:—

<sup>1</sup> *Archief*, 1918, 2, 807.

<sup>2</sup> At all events in the tropics.

<sup>3</sup> It appears that the period of vulcanization chosen for the different samples was such as to give approximately the "optimum" cure. Hence, it might be suggested that the conclusion as to the length of the resting period will apply only to the optimum cures, since other cures may require a longer period of rest. In view of the results which emerge from the discussion, in Chap. XV, of ageing, it is probable, however, that the conclusion applies to all cures.

TABLE LXXXIV

Period of rest . . .	24 h.	48 h.	72 h.	96 h.	120 h.
7 samples smoked sheet	1.38	1.37	1.38	1.38	1.39
9 „ latex crêpe .	1.32	1.32	1.31	1.315	1.31
7 „ lower grades .	1.34	1.34	1.33	1.36	1.35
Mean . . . .	1.345	1.34	1.34	1.35	1.35

Thus the differences in the tensile strength, as determined 1, 2, 3, 4 or 5 days after vulcanization, are inappreciable.

The position of the stress-strain curve was found to be appreciably, but only very slightly, affected by differences in the period of rest within the limits mentioned. The curve as determined after a longer period of rest occurred slightly lower on the paper than as determined after a shorter period of rest. Expressing the position of the curve by giving the percentage length at a load of 1.30 kg./mm.<sup>2</sup>, the position of the curve after periods of rest of more than 24 hours was lower by lengths summarized in the following table:—

TABLE LXXXV

Period of rest . . . .	Diminution in percentage length at 1.30 kg./mm. <sup>2</sup> .				
	24 h.	48 h.	72 h.	96 h.	120 h.
7 samples smoked sheet .	0	4	7.5	11.5	13.5
9 „ latex crêpe .	0	1	0.5	1	3.5
7 „ lower grades .	0	5	5	10.5	9.5

Hence, the extent to which the stress-strain curve altered on increasing the period of rest from 1 day to 3 or 4 days was no more than that represented by a diminution of length of, say, 5 to 10 per cent. at a load of 1.30 kg./mm.<sup>2</sup>, which would be interpreted as an increase in the time of cure of 2 to 3 minutes—say, 2–3 per cent. The data further showed that the results obtained after a rest period of 24 hours were certainly not less regular among themselves than the results obtained after a longer rest. This conclusion was confirmed by a further experiment specially directed to the point.

Less extensive data given by Eaton<sup>1</sup> are in general agreement

<sup>1</sup> *Loc. cit.*, p. 40.

with the above conclusions. The periods of rest in Eaton's experiments included a shorter period than the shortest period mentioned above—namely, 2 hours. The other rest periods examined were 1, 2 and 3 days. Samples of rapid- and of slow-curing rubbers were compared at a number of different states of cure. The results obtained after a rest of only 2 hours were generally markedly different from the results obtained after one of the longer rest periods; but the difference between the results after 1, after 2 or after 3 days' rest were very small. The curves both for the rapid- and for the slow-curing samples altered between 2 hours and 1 day by an interval corresponding to an extra cure of from 2 to 3 minutes. Between 1 day and 3 days the change in the position of the curve was negligible.

When a sample of a rubber-sulphur compound is removed from the vulcanizer at the conclusion of vulcanization, it is transparent and generally dark brown in colour. As it cools, it becomes opaque and lighter in colour, due presumably to the separation in solid form of the free sulphur, which at the temperature of vulcanization was liquid. The appearance of the vulcanizate can be observed to be undergoing change for some time. It would appear, from the results noted above, that the change is not complete after 2 hours but may be regarded as complete after 24 hours.

Eaton suggests that in the cases of mixes containing a smaller proportion than those examined above, the period of rest required may be shorter owing to the free sulphur being smaller in amount.

## CHAPTER XIII

### PROGRESSIVE CHANGES ON VULCANIZATION

THE changes brought about by vulcanization or, as it is frequently called, curing, are progressive. As a first example of the progressive nature of the vulcanization process, the following results<sup>1</sup> on the insolubility produced in rubber by vulcanization may be quoted. A sample of rubber was mixed with sulphur in the proportion 92.5 : 7.5, and was vulcanized at 148° for periods indicated below. After the extraction of "free" sulphur from the products by means of acetone, 2 g. of each was shaken with 100 c.cs. of benzene for twenty-five hours. The benzene was found to dissolve the quantities, expressed as percentages of the material taken, shown in the following table.

TABLE LXXXVI

Time of heating (mins.) .	5	10	20	40	60	80
Combined sulphur in product (per cent.) . . .	—	0.85	1.09	1.60	2.18	2.82
Percentage of product dissolved by benzene .	96.6	75.2	30.2	10.0	7.2	4.6

The product obtained on heating a mixture of rubber and sulphur may exhibit characters ranging from those exhibited by the soft, uncured "dough" to those exhibited by the hard material, ebonite.<sup>2</sup> The factors involved in the vulcanization of a sample of rubber which predominantly influence the character of the product are (a) the length of the period of heating (the time of cure), (b) the temperature, (c) the proportion of sulphur employed.<sup>3</sup> The progressive change in the character of

<sup>1</sup> Van Heurn, *Meded. Delft*, 1916, p. 410; *Delft Communics.*, p. 220.

<sup>2</sup> Ebonite, otherwise known as "hard rubber," is obtained by employing a much larger proportion of sulphur and a much longer period of heating than are employed in the production of soft rubber.

<sup>3</sup> Such factors are the controllable factors in vulcanization. The uncontrollable factor (or factors) is what may be denominated the *vulcanizing quality* of the sample of rubber in question. (This is uncontrollable, of course, only if the rubber is regarded as *given* at this point. It is not, as will have been clear from Part I, uncontrollable in the same way if the latex is *given*.)

the product following progressive change in the above factors displays itself most characteristically in (a) the tensile properties, (b) the condition of the sulphur. Before approaching more closely the important question of the methods by which the quality of different samples of rubber may be judged, it is desirable that the influence on the character of the product of the three factors mentioned above, as displayed in the two ways also mentioned above, should be examined in some detail.

#### "FREE" AND "COMBINED" SULPHUR

Prior to vulcanization the whole of the sulphur which has been mixed with a sample of raw rubber can be extracted by acetone. After vulcanization some of the sulphur is no longer extractable by acetone. Vulcanization brings about a change in the condition of some, or, exceptionally, of all, of the sulphur, which exhibits itself in the first place in a change from solubility to insolubility in acetone. The two conditions of the sulphur, which are recognized analytically by means of extraction with acetone, are known as "free" and "combined" sulphur. Following a suggestion of C. O. Weber's, the amount of "combined" sulphur in a given vulcanizate is generally expressed as a percentage of the rubber present and designated the *Coefficient of Vulcanization*.

The combined sulphur is held by the vulcanizate with extraordinary tenacity. Although the preparation of "Reclaimed Rubber" has been conducted industrially for many years, and has been the subject of a large amount of experimentation, the actual reclaiming or de-vulcanizing of rubber in the sense of removing the combined sulphur has never been achieved (except in the very recent work of Spence and of Dubosc).<sup>1</sup> In the

<sup>1</sup> *De-vulcanization*.—The successful removal of combined sulphur appears to have been achieved by Spence (*U.S. Pat. No. 1,235,850* of 1917), and by Dubosc (*Le Caoutchouc*, 1918, **15**, 9568, 9588; 1919, **16**, 9721, 9732). Both have proceeded on the principle of employing for de-vulcanization reagents which act as strong catalysts in vulcanization. The latter has experimented with hexamethylenetetramine. In one experiment 83 per cent. of the combined sulphur of a sample was removed by heating in an autoclave for twenty-four hours at seven atmospheres pressure with a saturated solution of hexamethylenetetramine.

Spence gives the following account of the line upon which he approached the question: "Vulcanization of rubber by sulphur is a reaction the velocity of which can be accelerated, and to be technically successful requires an accelerator to facilitate the reaction. The more powerful the accelerator employed, the more violent and complete will be the reaction."



industrial preparation of "reclaimed" or "regenerated" rubber, the removal of the free sulphur only is achieved.

Vulcanized rubber may be subjected to a large variety of severe treatments; but it will still be found when the rubber is recovered that it has retained the whole of the combined sulphur which it held prior to the treatment. Recent examples of such treatments may be found in experiments made by Repony.<sup>1</sup> For example: treatment of ordinary "regenerated" rubber with powdered sodium hydroxide, lead oxide, lead acetate or iron oxide at 170° for twelve hours in a digester; treatment of rubber dissolved in kerosene with zinc powder and hydrochloric acid; treatment with sodium hydroxide and aluminium or zinc powder; treatment with metallic sodium.

While the analytical distinction between "free" and "combined" sulphur can be made, in the way already stated—with acetone—with definiteness,<sup>2</sup> it is not yet possible to state with

---

Without such an accelerator the vulcanization of rubber proceeds very slowly, even at high temperatures, whereas in the presence of even a trace (0.01 per cent.) of a suitable accelerator, vulcanization of rubber by sulphur can be effected in a few minutes. It therefore appeared that the true solution of the problem of effecting a real de-vulcanization must lie in the use of a powerful vulcanization accelerator in conjunction with an element capable of combining with and fixing the sulphur liberated from the rubber by the accelerator."

As an accelerator in this connection, aniline, a substance which has the advantage of being a solvent for rubber, is most prominently mentioned by Spence; and, as the agent for fixing the sulphur, metallic potassium. The latter is employed in quantity equal in weight to the quantity of rubber treated. It is stated, as an example of the results to be obtained, that five parts of extracted hard rubber dust containing originally 32 per cent. of combined sulphur, after being heated for five hours at 175° in an autoclave with 300 parts of aniline containing five parts of potassium, gave a product which, after being isolated in a suitable manner, was found to be soluble in chloroform and in benzene and to contain only 8.9 per cent. of combined sulphur, 73 per cent. of the combined sulphur originally present having been removed.

<sup>1</sup> *I.R.W.*, 1917, p. 390.

<sup>2</sup> When propounding his adsorption theory of vulcanization (see later), Wo. Ostwald maintained that there was no sharp dividing-line between free and combined sulphur: that sufficiently prolonged extraction would remove the latter. Spence, however, showed that there was a definite limit to the amount of sulphur which could be extracted from a vulcanizate by acetone, and that the difficulty in reaching finality in the extraction was due to the fact that the free sulphur is present in an adsorbed condition. That a sufficiently definite distinction can be made between free and combined sulphur has been generally accepted by workers on the subject.

Mention should, however, be made of results reported by Harries and Fonrobert (*Ber.*, 1916, 49, 1196, 1390). These authors vulcanized a sample of rubber for thirty minutes at 145°, and extracted the product with hot acetone for a period of sixty days. They found that finally the sulphur-content of the product was only 0.25 per cent. (One experiment only is

any feeling of certainty what is the more intimate distinction between sulphur in the two forms. It may be said that the general trend of opinion is to the view that the combined sulphur is in veritable chemical combination with caoutchouc and not merely in physical association with it. But even if such a view be accepted, the question of the distinction between free and combined sulphur has a wider sweep. It takes in the whole question of the nature of the chemical and physico-chemical changes which may characterize vulcanization.

*The nature of vulcanization.*—It cannot be said that we are yet within sight of any complete or satisfactory understanding of the intimate nature of the vulcanization process. And it is not proposed to enter here into the question at any considerable length.

In the theory of vulcanization first to be formulated (Weber's), the process was regarded as essentially chemical. In the next theory to be propounded (Ostwald's) it was regarded as essentially physical. But it may now be considered as highly probable that vulcanization cannot adequately be viewed as merely a chemical reaction or as merely an adsorption process. It is not improbable that vulcanization involves considerations of chemical reaction, adsorption, polymerization and (possibly) catalysis; waiving the question as to whether one of these, and if so, which, is fundamental.

---

given.) They supposed that had the extraction been continued still longer the sulphur would have been removed entirely.

Stevens (*J. Soc. Chem. Ind.*, 1919, **38**, 192 T) has traversed the work of Harries and Fonrobert. He vulcanized samples of ordinary and of rapid-curing rubber under the conditions described by Harries and Fonrobert, except that the rubber was in the form of thin sheets, 0.5–1 mm. thick, and not, as apparently in Harries and Fonrobert's experiments, in thicker slabs. (Stevens regards such slabs as unsuitable, in view of the poor thermal conductivity of rubber.) It was found, in complete disagreement with Harries and Fonrobert, that there was a sharp distinction between free and combined sulphur in the vulcanizate. Such a distinction was also found even when the time of vulcanization was only nineteen minutes. Thus, in the sample which showed the lowest percentage of combined sulphur, the sulphur remaining in combination after two weeks' extraction with boiling acetone was 0.67 per cent., and after nine weeks' extraction 0.70, *i. e.* extraction with acetone had reached its limit after two weeks only. Stevens concludes that Harries and Fonrobert must have been working with "an excessively slow vulcanizing and inferior quality of rubber, or that, owing to the thickness of the discs used and the short time of vulcanization, or for some other reason, the rubber was only surface-vulcanized." Prior to Stevens' repetition of Harries' and Fonrobert's work, Twiss (*Rep. Progress Appd. Chem., Soc. Chem. Ind.*, 1918, **3**, 320) had suggested that the latter's results were due to the occurrence of oxidation during the prolonged extraction.

The first attempt at a theory of vulcanization was that of C. O. Weber<sup>1</sup> in 1902.<sup>2</sup> Vulcanization was regarded as due essentially to the union of sulphur with unsaturated bonds in the caoutchouc molecule. It was suggested that there existed a series of compounds (polyprene sulphides), ranging from  $(C_{10}H_{16})_{10}S_2$  to  $(C_{10}H_{16})_{10}S_{20}$ , and formed as vulcanization progressed from the stage of soft rubber to the stage of ebonite. Weber concluded from his experimental work that, no matter how much sulphur was present, and no matter how far heating was prolonged, no more sulphur than that—32 per cent.—corresponding to the latter compound could enter into combination.

Some years later (1910) Wo. Ostwald put forward a theory in which vulcanization was regarded as a process of adsorption of sulphur by caoutchouc. The amount of exact experimental data on the kinetics of the reaction between rubber and sulphur available at the time was only meagre; and Ostwald's theory, while it has had the merit of stimulating further investigation of the vulcanization process, is now to be recognized as—except, possibly, in some very much modified form—untenable; although it is not improbable that adsorption plays some part in the vulcanization process.

Ostwald supposed that the final result of continued vulcanization with a given proportion of sulphur would be an adsorption equilibrium between adsorbed ("combined") and unadsorbed ("free") sulphur. Spence and his collaborators, in a series of papers from 1911 to 1913,<sup>3</sup> showed the improbability of the existence of such an equilibrium. They found that, within the limits of sufficiency of the analytical methods employed, the whole of the sulphur mixed with rubber could enter into combination—at all events when its amount did not exceed 32 per cent. They showed, further, that the temperature coefficient of the process, considered in regard to the combination of sulphur, was similar to that laid down by van't Hoff as characteristic of a chemical reaction, and not, as Ostwald had supposed, similar to that characteristic of adsorption. The conclusions of Spence

<sup>1</sup> *The Chemistry of India-Rubber*, London, 1902; *Grundzüge einer Theorie der Kautschukvulkanisation*, Dresden, 1902; *Gummi-Ztg.*, 1902, 16, 561.

<sup>2</sup> The date of this first theory of vulcanization may be remarked as indicating to what a late date the rubber industry remained almost entirely empirical.

<sup>3</sup> *Koll. Zeit.*, 1911, 8, 304, 9, 83, 300; 1912, 10, 299, 11, 28, 274; 1913, 13, 265.

as to the absence of a final position of equilibrium in regard to the combination of sulphur other than total combination and as to the magnitude of the temperature coefficient have been amply confirmed by subsequent workers—Fol and van Heurn,<sup>1</sup> Eaton and Day,<sup>2</sup> de Vries.<sup>3</sup>

As mentioned elsewhere, Ostromislenski has found that a number of organic compounds, particularly trinitro-aromatic compounds and organic peroxides, are capable of producing in rubber a change which, although, according to investigations by Stevens and Bunschoten, not associated with mechanical properties as good as those of rubber vulcanized with sulphur, is substantially similar to that brought about by sulphur. From a consideration of this fact, Ostromislenski has suggested a view of the vulcanization process which regards it as involving both chemical reaction and adsorption. He supposes that the various agents which may bring about vulcanization first react chemically with a small portion of the rubber, and that the derivative thus formed is then adsorbed by the larger and unchanged portion of the rubber. As the chemical derivative may in different cases be produced by different agents, the adsorption of the derivative by the mass of the rubber is, it would seem, to be regarded as the *characteristic* feature of the vulcanization process. In support of his view, Ostromislenski states<sup>4</sup> that he has produced actual vulcanization by using as the vulcanizing agent caoutchouc bromide or hydrochloride.

It must be stated that a complete and substantiated theory of vulcanization cannot yet be given, although a considerable number of suggestive investigations have been devoted to the subject by a number of workers. Particular mention may be made of the investigations of Spence and his co-workers,<sup>5</sup> emphasizing the chemical aspect of the vulcanization process; of Skellon,<sup>6</sup> viewing the combination of sulphur with rubber from the point of view of mass action; of Kirchhof,<sup>7</sup> studying change in viscosity, as an index to change in the state of aggregation, in rubber solutions containing sulphur chloride; of Ostromislenski, presenting a number of novel points of view. A useful

<sup>1</sup> *Meded. Delft*, 1916, p. 330; *Delft Communics.*, p. 183.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1917, **36**, 16, 1116.

<sup>3</sup> *Meded. van het Centraal Rubberstation*, No. 1.

<sup>4</sup> *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1898 (*J. Soc. Chem. Ind.*, 1916, **35**, 370; *Chem. Soc. Abstrs.*, 1916, i, 278); *U.S. Pat.* 1,242,586 of 1917.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Koll. Zeit.*, 1914, **14**, 96; *Rubber Industry*, 1914, p. 172.

<sup>7</sup> *Koll. Zeit.*, 1914, **14**, 35.

critical review of investigations directed to revealing the nature of the vulcanization process is given by van Iterson.<sup>1</sup>

#### DETERMINATION OF THE COEFFICIENT OF VULCANIZATION

While a discussion of the analysis of the often-complex mixtures which constitute technical rubbers would be beyond the scope of the present volume, it is desirable that an analytical operation of such importance in regard to the investigation of vulcanization as the determination of the vulcanization coefficient should be given some attention. For the purpose of arriving at a figure for the coefficient of vulcanization in a rubber-sulphur vulcanizate,<sup>2</sup> either the combined sulphur may be estimated directly after exhaustive extraction of the sample with acetone, or the total sulphur (in the unextracted sample) and the free sulphur (in the acetone extract) may be estimated and the combined sulphur obtained by difference. In the latter case, where a series of vulcanizates from the same mix are in question, the total sulphur in the mix may be estimated once and for all—or, less satisfactorily, may be taken from the known quantity of sulphur put in the mix.

*Estimation of free sulphur.*—The estimation of free sulphur does not offer any serious difficulties. The material in hand—the acetone extract after removal of the solvent—consists largely of pure sulphur and contains only a small amount of organic matter. It is oxidized comparatively readily with nitric acid and bromine. The following is the procedure recommended by the Bureau of Standards:<sup>3</sup>—

“Add to the flask containing the acetone extract uncorrected 50–60 c.c. of distilled water and 2 or 3 c.c. of bromine. (If the acetone extracted indicated a large amount of free sulphur, the amount of bromine used may be increased.) Heat

<sup>1</sup> *Meded. Delft*, 1916, p. 155; *Delft Communics.*, p. 239. Van Iterson suggests that the central factor in vulcanization may be the presence of a certain modification of sulphur which is particularly active in the reaction with caoutchouc; so that, say, the velocity of vulcanization may be determined by the rate of the inversion  $S\lambda \rightleftharpoons S\mu$ . Cf. Erdmann's view (*Annalen*, 1908, 362, 169) regarding the importance of thiozone molecules ( $S_3$ ) in vulcanization. Cf. also Twiss (*J. Soc. Chem. Ind.*, 1917, p. 788), comparing vulcanization by the soluble variety of sulphur with vulcanization by the insoluble variety. The former variety entered into combination slightly faster than the latter.

<sup>2</sup> Concerning the determination of the vulcanization coefficient in mixes containing inorganic additions, such as litharge, which are capable of themselves fixing sulphur, see p. 389.

<sup>3</sup> *Bureau of Standards' Circular*, No. 38, 3rd edition, 1915, p. 66.

gently on the steam bath until the solution is practically colourless, and filter into a 250-c.c. beaker. Cover the beaker with a watch glass, heat to boiling on the steam bath, add 10 c.c. of 10 per cent. barium chloride solution, and allow the precipitate to stand overnight."

In the present writer's experience bromine is a satisfactory agent for the oxidation of the acetone extract.

The Delft Institute employs the procedure of Frank and Marckwald,<sup>1</sup> in which nitric acid alone is used for the oxidation. It states, however, that, as the oxidation is incomplete if the percentage of sulphur is at all considerable, "when the sulphur is above 1 per cent. it is better not to use this method, but to calculate the amount of free sulphur from the difference of the total sulphur and the combined sulphur."

Eaton and Day<sup>2</sup> follow treatment with nitric acid and bromine by fusion with a mixture of 1 potassium chlorate : 6 fusion mixture. Potts<sup>3</sup> shows that, unless the oxidation of sulphur by fuming nitric acid is constrained to proceed gently, a serious loss of sulphur may occur, due presumably to its being carried away in fine spray. In an experiment, in which quantities of 0.1000 g. of sulphur were treated, in beakers covered with clock glasses, with 20 c.cs. of fuming nitric acid, a comparison was made between the effect of heating the beaker by placing it on the top of a boiling-water bath and heating it by placing it half in the water. The barium sulphate obtained in estimations, using these two heating methods, was respectively 98-99 and 87-89 per cent.; the loss of sulphur in the more vigorous oxidation being about 12 per cent. In two further estimations in which the oxidation was conducted still more gently, a clock glass being interposed between the bottom of the beaker and the steam, the results were 98.7 and 100.1 per cent.

*Estimation of total and of combined sulphur.*—The estimation of total sulphur or of combined sulphur offers more difficulty than the estimation of free sulphur, owing to the association of the sulphur with a large amount of organic matter. Heating in a sealed tube, as in the Carius method of estimating sulphur in organic compounds, is not generally employed. The procedures used depend in general on oxidation in an open vessel with two or more agents—applied simultaneously or successively

<sup>1</sup> *Delft Communics.*, p. 145.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 128.

<sup>3</sup> *Rubber Industry*, 1911, p. 336.

—such as fuming nitric acid, bromine, potassium nitrate, potassium chlorate. A method of estimating sulphur on such lines was developed by Henriques,<sup>1</sup> a pioneer in the analysis of rubber goods. Since then a large number of different methods, presenting a general similarity, but differing in the exact lines of procedure, have been published.<sup>2</sup> A critical examination of a number of them has been published by Waters and Tuttle.<sup>3</sup>

The Delft Institute<sup>4</sup> states that, after investigation of many of the numerous methods proposed, it selected as most satisfactory the method of Rothe,<sup>5</sup> according to which the sulphur is oxidized and the organic matter destroyed by means of fuming nitric acid in the presence of magnesium nitrate. It is stated that confirmatory "tests with pure sulphur gave fairly accurate results, which was not the case with many other methods. Nevertheless, greater accuracy is not to be expected than within 0.2 to 0.3 per cent. of sulphur, and errors as high as 0.5 per cent. are not excluded."<sup>6</sup>

For the oxidation of total sulphur the Bureau of Standards<sup>7</sup> recommends treatment of 0.5 g. of rubber with 20 c.cs. of nitric acid-bromine mixture in a large crucible, followed, after evaporation, by fusion with 5 g. of a fusion mixture (equal parts of sodium carbonate and potassium nitrate).<sup>8</sup> This method, like probably the majority of the methods which have been proposed, involves heating with a fusion mixture; and from this circumstance errors in the barium sulphate precipitation are not unlikely. The work of Allen and Johnston<sup>9</sup> has shown to what an important

<sup>1</sup> For Henriques' papers on rubber analysis, see *Chem.-Zig.*, 1892, **16**, 1595, 1623; 1893, **17**, 634, 707; 1894, **18**, 441, 905; 1895, **19**, 235, 382, 403, 2043; *Zeit. angew. Chem.*, 1899, **34**, 802.

<sup>2</sup> Cf. Pontio, *Analyse du caoutchouc et de la Gutta-Percha*, Paris; Hinrichsen and Memmler, *Der Kautschuk und seine Prüfung*, 1910; Caspari, *India-Rubber Laboratory Practice*, 1914; R. Ditmar, *Die Analyse des Kautschuks N.S.W.*, Wien u. Leipzig, 1909, p. 187 *et seq.*

<sup>3</sup> *Bull. Bureau of Standards*, 1912, **8**, 445; *J. Ind. Eng. Chem.*, 1912, **3**, 734.

<sup>4</sup> *Delft Communics.*, p. 144.

<sup>5</sup> Cf. Hinrichsen and Memmler, *op. cit.*, 140.

<sup>6</sup> Cf. results tabulated by Fol and van Heurn (*Meded. Delft*, 1916, p. 331) comparing free sulphur as determined directly in the acetone extract and determined from (total sulphur—combined sulphur by Rothe's method). The latter is in all cases higher than the former figure for free sulphur, showing that combined sulphur as determined by oxidation with nitric acid and magnesium nitrate is too low.

<sup>7</sup> *Loc. cit.*, p. 66.

<sup>8</sup> The present author's experience with this method is not entirely favourable. And the mortality among the crucibles is liable to be high.

<sup>9</sup> *J. Amer. Chem. Soc.*, 1910, **32**, 588. Cf. also Kriebel and Mangum, on the difficulties arising in connection with the estimation of sulphur in foods by the use of a sodium carbonate-sodium peroxide fusion, *ibid.*, 1919, **41**, 1317.

extent the estimation of sulphur by precipitation with barium chloride may be rendered erroneous by the presence of large quantities of other salts. The influence of such quantities of salts as are present in the liquid, containing sulphate, derived from a fusion for total sulphur in rubber has been examined by Potts.<sup>1</sup> Potts found the error in the percentage of sulphur in four experiments to be — 0.10 on 1.6 per cent, — 0.03 on 4.0 per cent, — 0.03 on 8.0 per cent, — 0.13 on 16 per cent. He concluded that the influence of the potassium nitrate derived from the fusion mixture in reducing the weight of the barium sulphate precipitate could be compensated by the addition to the liquid of potassium chloride in four times the weight.

In the present writer's experience the wet method of Rosenstein and Davies<sup>2</sup> gives checks within 0.1 per cent. In this method oxidation is brought about by nitric acid, with the assistance of bromine water and potassium chlorate, in the presence of a strong solution of arsenic acid of boiling point 140°. The function of the arsenic acid solution is to raise the temperature at which oxidation can be conducted. In a method described by Kratz, Flower and Coolidge,<sup>3</sup> in which the same oxidizing agents are used, a solution made by dissolving 200 g. of zinc in 1 litre of concentrated nitric acid serves the same purpose as the arsenic acid in the Rosenstein-Davies method.

Eaton and Day,<sup>4</sup> who report that they found unsatisfactory methods for the estimation of sulphur (total and combined) involving the use of nitric acid, bromine and alkaline fusion, have, for the estimation of combined sulphur in vulcanizates containing 10 parts of sulphur to 90 parts of rubber, employed, with good results, a combustion method, which is a modification of one described long ago by Reinhardt.<sup>5</sup> They concluded that the absorbing agent employed by Reinhardt, viz. brominated hydrochloric acid, failed to arrest all the sulphur compounds formed, as also, without the use of platinized asbestos, did the agent suggested by Gaunt,<sup>6</sup> viz. hydrogen peroxide. They found, however, that all the sulphur compounds were

<sup>1</sup> *Rubber Industry*, 1912, p. 336.

<sup>2</sup> Davies, *Chemist Analyst*, No. 15, Oct. 1916; *Le Caoutchouc*, 1916, 9095; *I.R.J.*, 1919, 57, 1100.

<sup>3</sup> *Jour. Ind. Eng. Chem.*, 1920, 12, 317.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1917, 36, 16; *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 122 et seq.

<sup>5</sup> *Moniteur Scientifique*, Quesneville, 15, Sept. 1885 (*Chem. News*, 1885, 52, 225).

<sup>6</sup> *Analyst*, 1915, 40, 9.



arrested by strong sodium hydroxide solution, even though the combustion were not assisted to completeness by the introduction of platinized asbestos into the combustion tube. On subsequent acidification of the sodium hydroxide solution with brominated hydrochloric acid, the whole of the sulphur in the rubber could be obtained as barium sulphate. Details of this method are given in a footnote.<sup>1</sup> Six or eight samples of rubber were

<sup>1</sup> *Eaton and Day's modification of Reinhardt's combustion method for the determination of total or combined sulphur.*—Quantities each weighing exactly 0.1374 g. (0.01 g. barium sulphate represents 1.0 per cent. of sulphur) are weighed out from crumbed samples and are wrapped up in small filter paper packets, which are marked in pencil for subsequent identification. The packets are stacked in bundles of six or eight, and are extracted in a Beadle and Stevens' soxhlet (*Analyst*, April 1913). Extraction with acetone is continued for 100 hours; the packets being opened three times, at intervals, and their contents teased out with a finely pointed glass rod and forceps. At the conclusion of the extraction the samples are allowed to dry in the air at ordinary temperature. The combustion of the samples is then carried out as follows:—

A strand of platinized asbestos is laid lengthways along the paper packet, which is then placed in a glass tube, sealed at one end, 3 cm. long and 1 cm. wide. The strand is sufficiently long to project from and to be looped back over the mouth of the tube. This precaution causes a quick, initial ignition and materially assists the last stages of the combustion. The tube and its contents are then placed in the combustion tube with the open end forward, *i.e.* nearest the absorption tubes, and about 8 cm. from the forward end of the combustion tube. The latter is of hard glass, 20 cm. long and 2 cm. wide. At the forward end it is drawn out to take a short piece of rubber tubing, which connects it to the absorption apparatus. The latter consists of two test-tubes, 15 cm. long by 1.5 cm. wide. The first contains 1.5 c.c. and the second 0.2 c.c. of 7-N aqueous sodium hydroxide. As a safeguard against the necessity of having to rush a rapid current of oxygen through if the combustion becomes a little violent, it is advisable to attach to the absorption tubes two small U-tubes filled with glass beads moistened with a little 2-N sodium hydroxide.

To effect the combustion, which occupies ten to fifteen minutes, a strong, roaring flame is applied to the combustion tube about 2 cm. in front of the small tube containing the paper packet of rubber, and a current of dry oxygen is passed slowly through the apparatus. This current is maintained until the paper commences to char, when, to minimize the chance of a small explosion spoiling the estimation, a stronger current of oxygen is passed—up to 200 c.c.s. per minute—until ignition occurs. The current of oxygen is then reduced and regulated so as to secure a small, bright flame with as little smoke as possible.

When only a white ash remains, the contents of the absorption tubes are washed into a 200-c.c. beaker. To the same beaker are added washings obtained from the combustion tube as follows: The large combustion tube is rinsed out with very dilute brominated hydrochloric acid, and the small tube is boiled in this solution until all the bromine is driven off. The liquid is then cooled and poured in the 200-c.c. beaker. The total bulk is then made up to 100 c.c.s. or over, and 5 c.c.s. of brominated hydrochloric acid (10 vols. conc. HCl, 10 vols. water, 1 vol. bromine) is added from a burette. The beaker is covered with a watch glass, agitated gently, and allowed to stand. After evaporating off the excess of bromine, filtering and making up to 50 c.c.s., the sulphate in solution is precipitated by 2 c.c.s. of a 10 per cent. solution of barium chloride. The filter paper and pre-

extracted with acetone at one time. Determinations of the combined sulphur present after extraction were made on each sample separately by combustion in a stream of oxygen; and, as a check, the total free sulphur in the samples was determined in the acetone extract. A large number of results are recorded by Eaton and Day. The total free sulphur and the sum of the combined sulphurs for the samples in any one group in all cases check very well.

#### PROGRESSIVE COMBINATION OF SULPHUR WITH CAOUTCHOUC

It is found that, keeping constant the temperature of vulcanization of a given mixture of rubber and sulphur, and gradually increasing the period of heating, there occurs a continuous increase in the coefficient of vulcanization. C. O. Weber, who first published data on the progress of the combination of sulphur with increasing period of cure, found discontinuities in the curve connecting the combined sulphur with the time. These "kinks" have figured to some extent in early discussions on the theory of vulcanization; but there is no doubt that their discovery in Weber's investigation was due to faulty technique; the autoclave being opened at intervals for the removal of a sample and then closed again. All subsequent workers have found the curve showing the combination of sulphur with increasing time to be continuous.

Spence and Young<sup>1</sup> found, for a mix of rubber and sulphur containing 10 per cent. of the latter, vulcanized at a constant temperature of 150° and at a constant temperature of 135°, that, until about 90 per cent. of the sulphur had entered into combination, the curve was a straight line. In one experiment in which more than 10 per cent. of sulphur, viz. 32 per cent., was used, they also found the curve to be a straight line up to the point at which about 28 per cent. of sulphur had combined.

With a rubber-sulphur mixture containing 7.5 per cent. of sulphur, Fol and van Heurn<sup>2</sup> also found the curve to be a straight line until the whole of the sulphur was combined. The following

---

cipitate are then dried and burnt in a muffle (there is no danger of reducing the sulphate to sulphide).

The course of the combustion, as observed by the author in Eaton's laboratory, was very satisfactory.

<sup>1</sup> *Koll. Zeit.*, 1912, **11**, 28.

<sup>2</sup> *Meded. Delft*, 1916, p. 330.

table shows the progressive increase in the combined sulphur observed by Fol and van Heurn:—

TABLE LXXXVII

Time (mins.)	0	10	20	30	60	90	120	180	240	360	480
Coeff. of vulcn.	0.19	0.91	1.09	1.65	2.75	3.69	5.49	6.89	7.70	7.61	7.62

Skellon<sup>1</sup> determined the rate of combination of sulphur with increasing periods of vulcanization in rubber-sulphur mixtures containing widely different percentages of sulphur. In one series of experiments vulcanization of rubber-sulphur mixtures containing 3, 5, 10, 20, 40 and 50 parts of sulphur, respectively, per 100 parts of rubber was conducted at 140°. A linear relation between combined sulphur and time was found in the case of the smaller proportions of sulphur, viz. 3, 5 and 10 parts. In the case of the larger proportions the curves were found to be S-shaped,<sup>2</sup> and not—as in the single series of Spence and Young with a high proportion of sulphur—straight lines.

Eaton and Day<sup>3</sup> determined the course of the combination of sulphur at 140° in rubber-sulphur mixings made with 10 per cent. of sulphur from three different types of rubber, namely: crêpe, sheet, slab. The data obtained are shown in Table XC (p. 321). The curing was continued until substantially all the sulphur had entered into combination. The number of intervals at which sulphur determinations were made was twenty-two or twenty-four. In the case of the crêpe rubber the curve connecting combined sulphur and time was practically a straight line up to the point at which 6–7 per cent. of sulphur was in combination. The curve for the sheet sample was approximately straight up to the point at which 5–6 per cent. of sulphur was in combination. Beyond these points the curves bent, showing a less rapid rate of combination of sulphur. The curve for the slab rubber had a very marked curvature. Now, of the three rubbers employed, slab is rapid-curing and the quickest of the three; crêpe is slow-curing and the slowest of the three. And Stevens<sup>4</sup> suggests that the explanation of the difference between, on the one hand, the slight curvature with

<sup>1</sup> *Koll. Zeit.*, 1914, 14, 96; *Rubber Industry*, 1914, p. 172.

<sup>2</sup> The curves in the case of the higher proportions of sulphur were almost coincident at the beginning of their course. This Skellon explains by supposing that the limited degree of solubility of sulphur in rubber, demonstrated by him, fixes a limit to the initial velocity of the reaction between rubber and sulphur. Cf. the remarks of van Iterson (*Meded. Delft*, 1916, p. 162; *Delft Communics.*, p. 245) on these curves.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Ann. Rep. Progress Appd. Chem.*, 1917, p. 348.

Eaton's crêpe and sheet samples and the very marked curvature with his slab sample, and on the other hand, the straight lines observed by Spence with a mix containing a similar proportion of sulphur is that the latter investigator used rubber which had been extracted with acetone, and thus partly deprived of accelerator, whereas the former investigator used non-extracted rubber containing the natural accelerator. That an explanation is to be sought on such lines is, it may be remarked, supported by observations of van Heurn,<sup>1</sup> from which it appeared that the curve connecting vulcanization coefficient and time was curved in the same sense as in the cases mentioned above, *i. e.* concave to the time axis, with mixtures of 92.5 parts of rubber : 7.5 parts of sulphur to which the accelerator, *p*-nitrosodimethylaniline, had been added. The curvature was greater when 0.5 per cent. than when 0.25 per cent. of the accelerator was present.

Kratz and Flower,<sup>2</sup> working with a mix consisting of plantation crêpe 100 : zinc oxide 100 : sulphur 5 : an organic accelerator 0.33 parts, find the relation between the combined sulphur and the time of cure to be represented by a line which is at first approximately straight, but which later bends over. Up to a vulcanization coefficient of a little more than two, corresponding to a cure somewhat beyond that giving the maximum tensile product, the curve approximated to a straight line (for data, see p. 388). These authors, working with the mix just mentioned, show how a series of steps of suitable length at increasing temperatures may be chosen, so that, by maintaining sufficiently the active mass of the sulphur throughout the course of the reaction, the relation between combination of sulphur and time may remain constant up to a higher vulcanization coefficient.<sup>3</sup>

#### PROGRESSIVE CHANGES IN TENSILE PROPERTIES

The change, with increasing period of vulcanization, in the tensile properties, particularly as indicated by the course of the

<sup>1</sup> *Delft Communics.*, p. 252.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1919, **11**, 30.

<sup>3</sup> It may be remarked that these authors also conclude that the tensile properties of a product cured to a given vulcanization coefficient by means of a series of rising temperatures may be better than those of a product cured to the same vulcanization coefficient at a constant temperature. It is not impossible that this conclusion may be of rather wide practical application. But it is to be noted that, in order to bring their point out clearly in the mineralized mix employed, Kratz and Flower have to cure to a vulcanization coefficient that admittedly represents a very marked over-cure. Cf. remarks in Chap. XVI on the smaller sensitiveness of mineralized mixes as compared with simple rubber-sulphur mixes.

stress-strain curve, was not made the subject of exact, quantitative study until, at a somewhat later date than that at which the exact investigation of progressive change in the vulcanization coefficient began, the fundamental importance for the evaluation of rubber of mechanical tests began to be appreciated. It may be said, speaking very broadly, that with the progress of the vulcanization of a given mix at a given temperature the breaking figures change in the following way: the length at break continually diminishes; the tensile strength continually increases, and then falls more or less quickly according to the character of the rubber and the vulcanizing conditions, until the product becomes, comparatively speaking, brittle, when it snaps at a small extension and small load.

This general statement may be illustrated by the following figure, in which it will be seen that (excluding from consideration

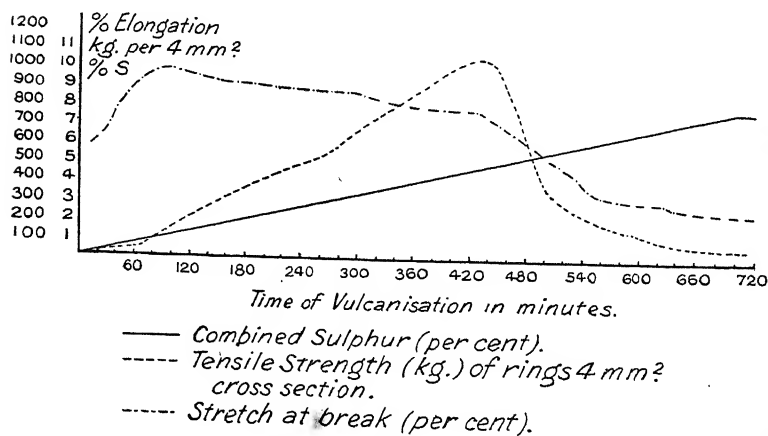


FIG. 23.

the initial period of pre-vulcanization, in which the elongation at break is rapidly changing from the figure characteristic of raw rubber to a figure for a vulcanized product) the graph representing the elongation falls continuously, whereas the graph representing the tensile strength rises gradually to a maximum and then falls comparatively rapidly. The figure represents results reported by Gottlob<sup>1</sup> for the vulcanization of a mixture of rubber 100 : sulphur 10 for increasing periods at a temperature of 138°.

<sup>1</sup> *Gummi-Ztg.*, 1916, 30, 303, 326.

The progressive change in the breaking figures with increasing time of cure will form the subject of fuller discussion in what follows, where the influence of the character of the rubber, the temperature of vulcanization, the proportion of sulphur and the presence of catalysts will be considered.

More important than a study of the progressive change of the breaking figures by themselves is a study of them jointly with a study of progressive change in the stress-strain curve. In Chap. X the stress-strain curve was considered, generally, in regard to the mechanical characters which it connotes; in the present chapter it will be considered in regard to the quality and state of cure of the vulcanizate giving a particular curve.

The stress-strain curves given by a number of samples of the same mix cured at the same temperature for increasing periods of time form a regular series, the members of which are of the same character and do not intersect. With loads taken horizontally and elongations vertically, the curves come down the paper in a regular fashion, as the period of vulcanization increases. The data in the following table and figure show for three different samples of rubber the breaking figures and the stress-strain curves recorded by Eaton<sup>1</sup> for a series of increasing times of cure at 140° in a mix rubber 90 : sulphur 10.

TABLE LXXXVIII

Time of cure (hrs.)	0.5	0.75	1	1.25	1.5	1.75	2	2.25	2.5	2.75	3	3.25	3.5	3.75	4.25
<b>A. Slab rubber—</b>															
P <sub>B</sub> . . .	0.58	0.86	1.08	1.42 <sup>r</sup>	1.45	0.53	0.54	0.24	—	—	—	—	—	—	—
L <sub>B</sub> . . .	1174	1100	1047	1027	973	735	706	528	—	—	—	—	—	—	—
<b>B. Sheet rubber—</b>															
P <sub>B</sub> . . .	—	—	—	—	0.86	0.96	1.10	1.40 <sup>r</sup>	1.41	1.05	0.38	0.25	—	0.17	0.17
L <sub>B</sub> . . .	—	—	—	—	1074	1045	972	986	925	825	612	504	—	380	344
<b>C. Crêpe rubber—</b>															
P <sub>B</sub> . . .	—	—	—	—	—	0.54	0.79	0.88	0.86	1.12	1.28 <sup>r</sup>	1.30	1.27	0.74	0.29
L <sub>B</sub> . . .	—	—	—	—	—	1030	1066	1048	1022	984	973	930	913	680	531

The cures giving Eaton's optimum cure are indicated by *x*. The vulcanization coefficients corresponding to these cures were 4.50 (at 1 $\frac{3}{8}$  hours), 4.20 and 4.00.

<sup>1</sup> *Loc. cit.*, p. 44. Similar series are given by Eaton and Grantham, *J. Soc. Chem. Ind.*, 1915, **34**, 989.

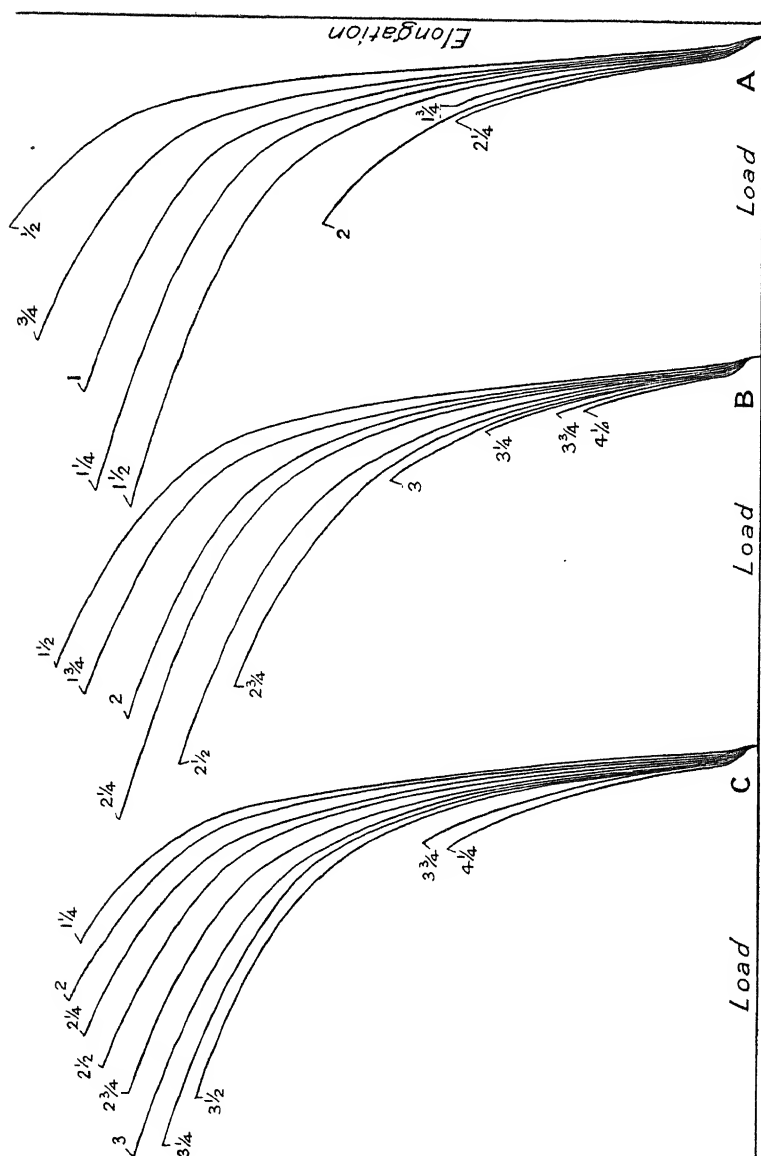


FIG. 24.

PROGRESSIVE CHANGE IN VULCANIZATION COEFFICIENT AND  
TENSILE PROPERTIES

A still more complete investigation, such as seems desirable in the present state of the question, of the progressive vulcanization of a given mix at a constant temperature will include examination of the progress of all three features to which reference has been made, namely: the breaking figures, the stress-strain curve, the vulcanization coefficient. The results for a case, carefully examined by de Vries,<sup>1</sup> in which attention was paid to all three features, are shown in the following table and figure. The breaking figures were determined with great exactness, fifty or so rings being tested for some of the cures. The necessity for testing a large number of test pieces in order to get perfectly reliable breaking figures will appear from the discussion, in the succeeding chapter, of the magnitude of the accidental errors affecting the determination of breaking figures.

TABLE LXXXIX

*Progressive cures at 148° of a mix of 92.5 rubber: 7.5 sulphur*

Time of cure (min.)	Rings tested.	Re-jected. <sup>2</sup>	P <sub>B</sub> .	L <sub>B</sub> .	L <sub>1.30</sub> .	Vulcn. coeff.	
						Per cent.	L <sub>1.3</sub> for sample analyzed.
60	14	0	0.40 $\frac{1}{2}$ $\pm$ 0.016 <sup>3</sup>	1079 $\pm$ 3.3 <sup>3</sup>	—	2.55	—
75	15	0	0.79 $\frac{1}{2}$ $\pm$ 0.014	1114 $\frac{1}{2}$ $\pm$ 4.8	ca. 1225	3.15	1225?
90	50	0	1.07 $\pm$ 0.009	1098 $\frac{1}{2}$ $\pm$ 1.3	1137 $\pm$ 1.4	3.77	1137
105	30	2	1.26 $\pm$ 0.008	1070 $\frac{1}{2}$ $\pm$ 1.7	1076 $\pm$ 1.7	4.38	1080
120	56	2	1.28 $\pm$ 0.008 $\frac{1}{2}$	1024 $\pm$ 1.4	1027 $\pm$ 0.7	4.99	1024
135	47	1	1.26 $\pm$ 0.011	977 $\pm$ 2.2	984 $\pm$ 1.1	5.44	985
150	11	6	1.17 $\pm$ 0.018	931 $\pm$ 3.4	953 $\pm$ 1.5	5.82	953
165	5	3	1.08?	894?	928?	—	—

It will be observed that the length at break falls continually, and that the breaking stress increases to a maximum and then falls. In the case of the above mix the change of the breaking stress in the neighbourhood of the maximum is only slow. The

<sup>1</sup> *Meded. van het Centraal Rubberstation*, No. 1, pp. 5-6; de Vries and Hellendoorn, *Archief*, 1918, 2, 770.

<sup>2</sup> Rejected because of flaws.

<sup>3</sup> The "probable error" is calculated from the formula  $0.845 \cdot \frac{\sum d}{n\sqrt{n-1}}$ .



stress-strain curves show the progress of vulcanization very distinctly. In the preceding table the position of the curves is expressed by giving the length (obtained by prolongation of

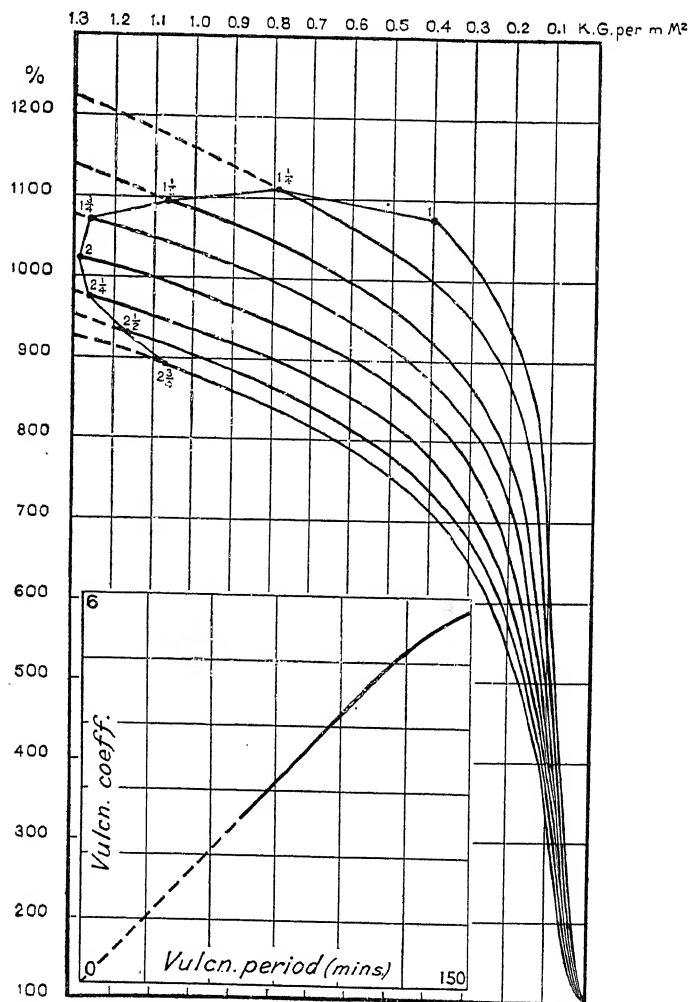


FIG. 25.—Stress-strain curves and average breaking-points for a sample cured for different periods of time.

the curves, as in Fig. 25) which would correspond to a load of 1.30 kg./mm.<sup>2</sup>. The ends of the curves, which represent the breaking-points, are joined together in Fig. 25. A curve

connecting the time of cure with the vulcanization coefficient has been constructed and inserted in the figure. It will be observed, in agreement with what has already been said concerning the combination of sulphur with time, that the curve is a straight line for most of its length, but bends slightly towards the end.

In the following table and figure are shown the vulcanization coefficient and tensile results for three rubbers of different types cured, by Eaton,<sup>1</sup> over a more extended range, viz. until practically all the sulphur had entered into combination. The composition of the mix was, rubber 90 : sulphur 10. The end points of the stress-strain curves indicate the breaking figures. As each end point is obtained from only one test piece, the course of the breaking figures is not as regular as would be the case if the breaking figures for each cure were taken as the mean of the figures for a number of test pieces.

TABLE XC

*Combined sulphur (per cent. on the vulcanized mix) for cures at ¼-hour intervals from 0-4 hours, ½-hour intervals from 4-5 hours, and 1-hour intervals from 5-10 hours*

0-3 hrs.	{ Slab (244 A)	0.29	1.29	2.22	2.91	3.63	4.44	5.06
	{ Sheet (244 B)	0.26	0.51	0.78	1.15	1.74	2.00	2.32
	{ Crêpe (244 C)	0.20	0.43	0.77	0.97	1.36	1.63	1.84
0-3 hrs. (continued)	{ Slab	. 5.47	6.19	6.96	7.22	7.54	8.03	
	{ Sheet	. 2.77	3.26	3.54	3.93	4.26	4.68	
	{ Crêpe	. 2.18	2.45	2.78	3.00	3.27	3.75	
3-10 hrs.	{ Slab	. 8.48	8.73	8.91	9.11	9.18	9.54	9.51
	{ Sheet	. 4.98	5.32	5.74	5.96	6.61	7.32	8.16
	{ Crêpe	. 4.05	4.38	4.90	5.02	5.57	6.10	7.32
3-10 hrs. (continued)	{ Slab	. 9.56	9.82					
	{ Sheet	. 8.71	9.06	9.28	9.55			
	{ Crêpe	. 8.30	8.87	9.48	9.63			

#### INFLUENCE OF TEMPERATURE

Increase of temperature hastens the vulcanization process. The curve connecting time and combined sulphur has a greater inclination to the time axis at a higher than at a lower temperature.

It has already been mentioned that the temperature coefficient of the vulcanization process, *i. e.* the factor giving the increase

<sup>1</sup> *Loc. cit.*

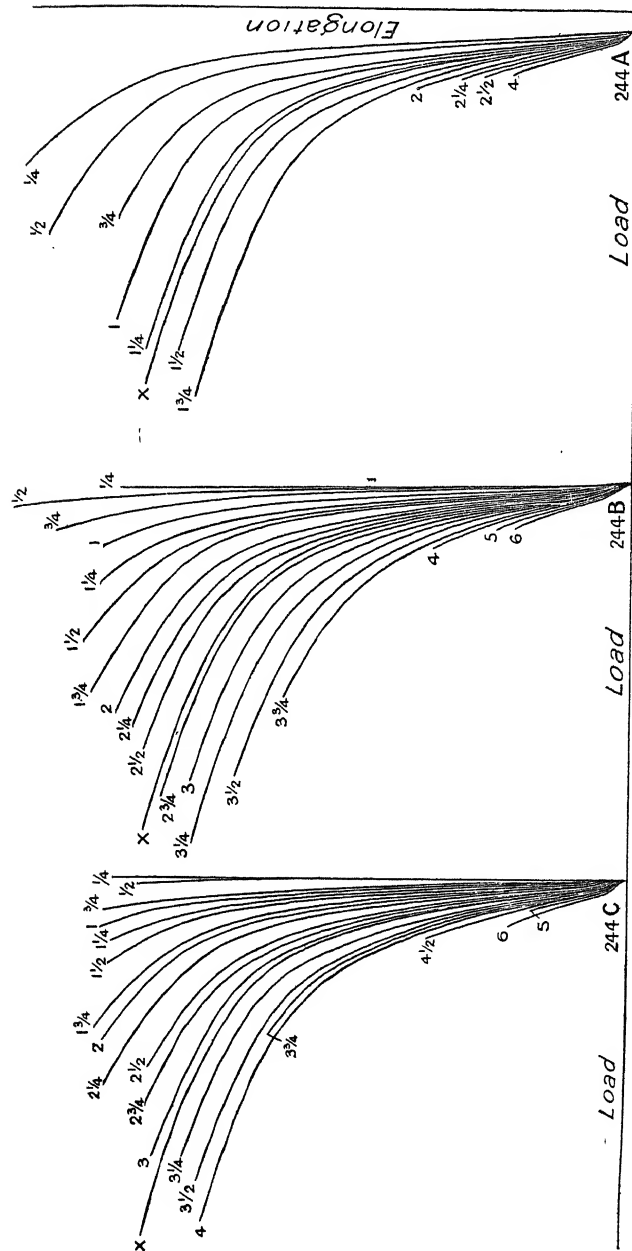


FIG. 26.1

1 Eaton's "optimum curve" (see later) has been drawn in these diagrams. It is indicated by x.

in velocity of combination of sulphur for an increase of  $10^{\circ}\text{C}$ . in the vulcanization temperature, is of the same order as the coefficient for a chemical reaction, viz. between 2 and 3. Spence and Young<sup>1</sup> found it, for rubber-sulphur mixes containing 10 per cent. of sulphur, to be 2.67 in the region of the usual vulcanization temperatures.<sup>2</sup> Fol and van Heurn,<sup>3</sup> as a result of comparing the vulcanization coefficients of portions of the same mix of rubber 92.5 : sulphur 7.5 vulcanized for  $1\frac{1}{2}$  hours at temperatures of 130, 145 and  $155^{\circ}$ , concluded that the temperature coefficient of the reaction was very close to 2. In the following further experiment by them it was found that a period of cure at  $147.1^{\circ}$  (3.5 atmospheres) gave, not only a similar vulcanization coefficient, but also similar breaking figures to double the period at  $138.1^{\circ}$  (2.5 atmospheres), *i. e.* at a temperature  $9^{\circ}$  lower. The breaking figures are the mean of tests on 9, or, in three cases, 7-8 rings.<sup>4</sup>

TABLE XCI

	1 h. at $147.1^{\circ}$ .	2 h. at $138.1^{\circ}$ .	1.5 h. at $147.1^{\circ}$ .	3 h. at $138.1^{\circ}$ .	2 h. at $147.1^{\circ}$ .	4 h. at $138.1^{\circ}$ .	2.5 h. at $147.1^{\circ}$ .	5 h. at $138.1^{\circ}$ .
Vulcn. coeff.	2.4	2.3	3.5	3.5	5.0	4.2	6.1	5.3
P <sub>B</sub> . .	0.602	0.643	1.01	0.904	1.295	1.10	1.42	1.39
L <sub>B</sub> . .	1065	1079	1023	1031	962	985	918	953

As regards the influence of the vulcanization temperature on the position of the stress-strain curve: the results just mentioned would suggest that for an increase of somewhat less than  $10^{\circ}$  in the vulcanization temperature, the stress-strain curve should come to the same position in about half the time. This is found

<sup>1</sup> *Koll. Zeit.*, 1912, 11, 28.

<sup>2</sup> Bourn ("A New Rule of Vulcanization," *Rubber Industry*, 1914, p. 411; *Le Caoutchouc*, 1913, 7864; *I.R.W.*, 1913, 47, 187) states that for the range of temperatures from  $194-337^{\circ}\text{F}$ . the velocity of vulcanization is doubled for each increase in temperature of about  $11^{\circ}\text{F}$ . ( $6^{\circ}\text{C}$ ). But the data given are quite insufficient to establish this statement.

<sup>3</sup> *Meded. Delft*, 1916, p. 340; *Delft Communics.*, p. 187.

<sup>4</sup> In an (unpublished) investigation in conjunction with O. J. Walker, the present author has found that the temperature coefficient of the reaction between rubber and sulphur appears to be uninfluenced by the presence of organic accelerators. For example, series of cures of a rubber-sulphur mix to which 1 per cent. of a powerful accelerator (the addition product of piperidine and carbon bisulphide) had been added were made at 130, 134.5 and  $141^{\circ}$ ; and it was found that the progress of vulcanization at  $141^{\circ}$ , as indicated by the vulcanization coefficient (and also by the tensile results), was, roughly speaking, three times as rapid as at  $130^{\circ}$  and not quite twice as rapid as at  $134.5^{\circ}$ .

to be the case in experiments made by de Vries.<sup>1</sup> Cures for a given time at 148° gave approximately the same position of the stress-strain curve as cures for double the time at 140°. The mixes were simple rubber-sulphur mixes. Lengths, measured in the case of each pair of cures at a suitable point, are recorded in the following table.

TABLE XCII

Sample.	Per cent. sulphur.	Period at 140° (h.).	Period at 148° (h.).	Length.		Load at which length measured (kg./mm. <sup>2</sup> ).
				140°.	148°.	
1G .	5	3	1.5	1200	1192	0.70
1H .	7	2	1	1194	1177	0.80
1H .	7	3	1.5	1079	1083	1.10
1M .	10	2	1	1073	1067	1.20
1M .	10	3	1.5	883	924	1.30
12B .	7.5	3.5	1.75	948	941	1.40
18 .	7.5	2.5	1.25	1130	1140	0.90

## INFLUENCE OF SULPHUR PERCENTAGE

The larger the proportion of sulphur in a rubber-sulphur mix, the further advanced, in a given period of vulcanization at a given temperature, will be the state of cure as indicated by the vulcanization coefficient, the breaking figures and the position of the stress-strain curve—at all events up to a proportion of, say, 10 per cent. of sulphur. The influence of the percentage of sulphur on the vulcanization coefficient and the breaking figures may be seen from the data, obtained by Fol and van Heurn,<sup>2</sup> given in the following table.

TABLE XCIII

*Mixtures of plantation crêpe and sulphur. All cured for 1.5 hrs. at 50 lb.*  
(Breaking figures are in most cases the mean of tests on 9 rings)

Per cent. sulphur in mix	2.5	5	7.5	10	12.5	15	17.5	20
P <sub>B</sub> . . .	0.29 <sup>3</sup>	0.63	0.99	1.24	0.57	0.23	0.25	0.62 (?)
L <sub>B</sub> . . .	1000	994	994	866	531	298	283	484
Vulcn. coeff. .	1.05	2.33	2.92	3.92	6.24	7.45	8.12	9.41

<sup>1</sup> *Meded. van het Centraal Rubberstation*, No. 1, p. 14.

<sup>2</sup> *Meded. Delft*, 1916, p. 346.

<sup>3</sup> Sample so soft that it had not broken by the time that the machine had gone to its limit of extension.

It appears that, for mixtures of an ordinary, non-rapid rubber, such as crêpe and sulphur, there is, for proportions of sulphur up to 15-20 per cent., approximate proportionality between the vulcanization coefficient and the proportion of sulphur present. This agrees with the results of Skellon, who found the curve connecting the vulcanization coefficient and the time to be markedly curved at the outset only when the proportion of sulphur was above 20 per cent.

The state of cure as shown in the tensile properties clearly advances with the proportion of sulphur present. The maximum breaking figures occur with 10 per cent. of sulphur; higher proportions of sulphur lead under the curing conditions in question to over-cures.

The change in the breaking figures in the experiment quoted above suggests that the stress-strain curve changes its position progressively with increase in the proportion of sulphur present. That in fact it does so is shown by tests, made by de Vries,<sup>1</sup> the results of which are given in the following table and in Fig. 27 overleaf.

TABLE XCIV

*Samples with different proportions of sulphur cured under the same conditions*

Sulphur (per cent. on mix)	5	7	7.5	8	9	10
P <sub>B</sub>	0.58	1.05	1.07	1.22	1.26	1.26
L <sub>B</sub>	1224	1116	1084	1064	1011	940

From the result of further tests<sup>2</sup> the same author concluded that, when the time of cure in the case of a rubber-sulphur mix containing 7.5 per cent. of sulphur was 1.5 times the time of cure in the case of such a mix containing 10 per cent. of sulphur (7.5 and 10 per cent. are proportions which have been considerably employed in experimental work), the stress-strain curves obtained were approximately coincident.

#### MAXIMAL TENSILE STRENGTH

With reference to the evaluation of rubber, the progressive changes brought about by increasing periods of cure may usefully be considered from the point of view of the *sharpness* with which a maximum displays itself in the tensile strength. The influence in this connection of the percentage of sulphur in the mix has been carefully examined by de Vries and Hellendoorn.<sup>3</sup> The

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ibid.*

<sup>3</sup> *Archief*, 1918, 2, 769.

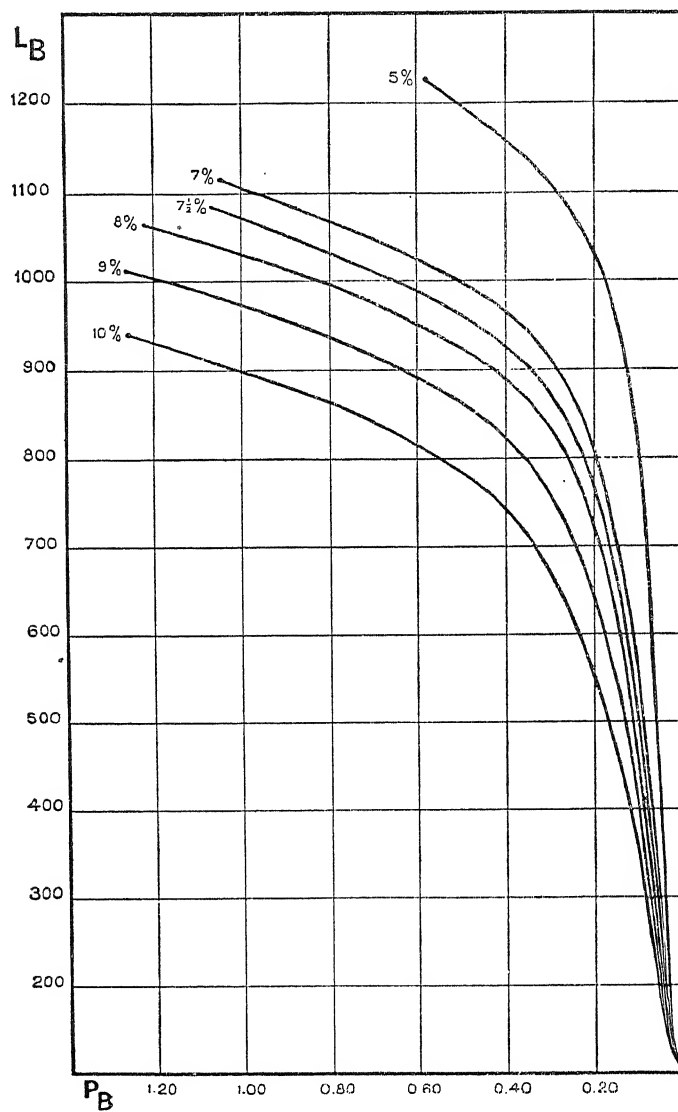


FIG. 27.—Stress-strain curves for the same sample of rubber cured under the same conditions with different proportions of sulphur.

vulcanization temperature was the same in all experiments, viz. 148°. The mix rubber 92.5 : sulphur 7.5 was examined first. It was concluded from tests on thirteen samples of rubber, all ordinary sheet or crêpe samples, that a maximum always occurs on curing such a mix at 148° for increasing periods of time. Three of the samples were examined particularly closely; the intervals of curing being only five minutes, and, in order to eliminate the possible influence of accidental errors in the breaking figures in producing irregularities, a large number of test pieces being tested. The results for one of these samples, in connection with which a total of 497 rings were tested, are given in the following table. The probable errors by which the breaking figures are affected are shown.

TABLE XCV

Sample 90

Period of vulcn. (min.)	Rings tested.	Re-jected for flaws.	P <sub>B</sub> .	L <sub>B</sub> .	L <sub>1-30</sub> .	Vulcn. coeff.	
						Per cent.	Sample used had L <sub>1-30</sub> .
75	20	0	0.75 ± 0.015	1091 ± 3.9	1210?	2.86	—
80	23	0	0.90 ± 0.014	1099 ± 2.2	1163?	—	—
85	29	0	1.02 ± 0.014	1090 ± 2.6	1140?	3.58	1145
90	58	1	1.145 ± 0.008	1092 ± 1.4	1118	3.77	1118
95	52	1	1.22 ± 0.009	1085 ± 1.4	1094	—	—
100	39	0	1.315 ± 0.009	1069 ± 1.8	1066.5	4.24	1070
105	38	2	1.345 ± 0.008	1057 ± 1.9	1050	4.47	1048
110	58	1	1.39 ± 0.008	1044 ± 1.6	1032	4.65	1026
115	50	2	1.405 ± 0.007	1028 ± 1.5	1013	4.85	1007
120	60	5	1.42 ± 0.006	1016 ± 1.0	998	5.07	1000
125	34	2	1.41 ± 0.008	1001 ± 1.6	985.5	5.30	985
130	28	0	1.39 ± 0.009	984.5 ± 1.5	971	5.49	976
140	4	0	1.37	958	945	—	—
150	4	0	1.30	925	925	—	—

The manner in which the breaking-point changes with progressive curing in the case of the three samples (Nos. 90, 13, 240) which were examined more exhaustively is shown in the following figure.

A preliminary comparison<sup>1</sup> of mixes, containing 5, 7.5 and 10 per cent. of sulphur respectively at half-hour curing intervals

<sup>1</sup> De Vries, *Meded. van het Centraal Rubberstation*, No. 1.



at 148°, had already shown broadly that the occurrence of a maximum in the tensile strength was sharper with a higher

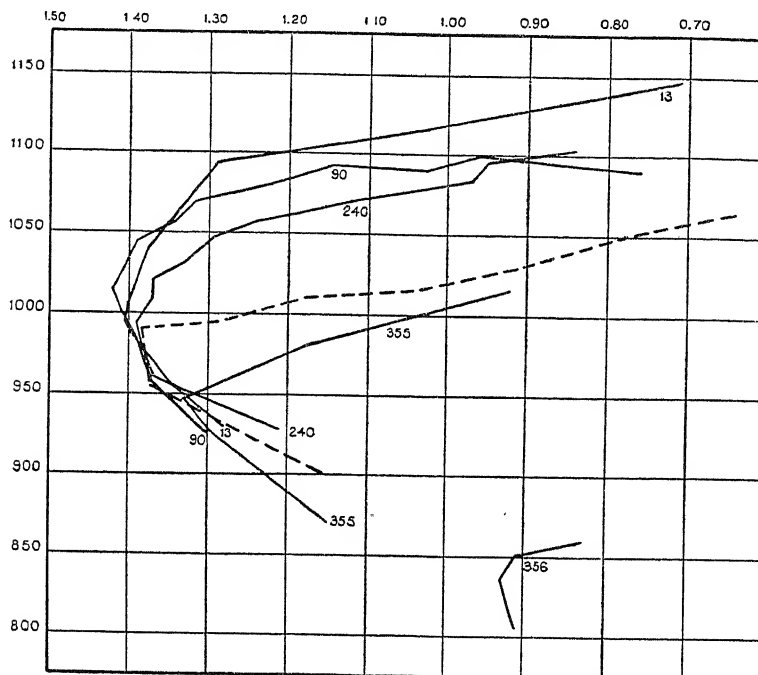


FIG. 28.—Curves of the breaking-points of five samples of rubber in different states of cure, together with the curve (the broken line) of the breaking-points for 341 samples cured by the Delft Institute under their standard conditions.

percentage of sulphur in the mix than with a lower one, as may be seen from the following table and figure.

TABLE XCVI

Period of vulcn. (hrs.)	1	1.5	2	2.5	3	3.5	4	4.5
P <sub>B</sub> { 5 per cent. sulphur	—	0.18	0.23	—	0.72	0.48	0.96	1.02
	7.5 " " "	0.27	0.44	0.75	0.96	1.07	—	0.89
	10 " " "	0.42	0.58	0.99	1.21	1.32	0.31	—
L <sub>B</sub> { 5 per cent sulphur	—	1196	1176	—	1206	1192	1168	1131
	7.5 " " "	1236	1175	1169	1137	1084	—	950
	10 " " "	1176	1105	1068	1011	920	562	—

Apparently the mix containing 5 per cent. only of sulphur had not attained its maximum tensile strength at the longest cure employed. The course of the results is not entirely regular, owing to the fact that only a small number of rings were tested at each cure. But it is clear that there is a sharp maximum in the tensile strength with 10 per cent. of sulphur, and a definite but flatter maximum with 7.5 per cent. The length at break diminishes with progressive vulcanization in the cases of 7.5 and of 10 per cent. of sulphur—more sharply in the latter case than in the former. In the case of 5 per cent. of sulphur the

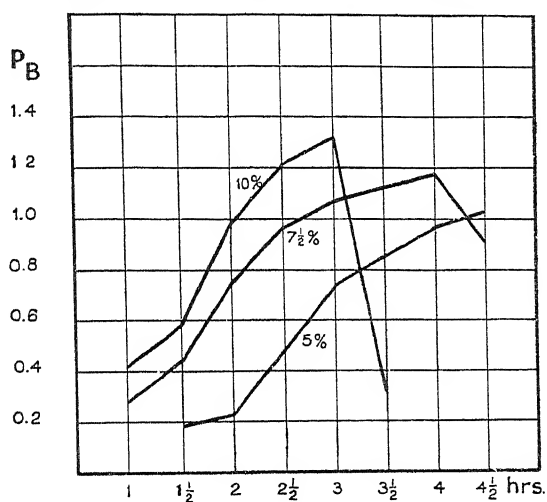


FIG. 29.

figures for the length at break are affected by irregularities. They show, however, that the length diminishes, but only slowly.

*Influence of proportion of sulphur on the sharpness of the maximum.*—A further examination, by de Vries and Hellendoorn, of rubber-sulphur mixes containing less than 7.5 per cent. of sulphur revealed some interesting points. With ordinary plantation rubbers cured for increasing periods at 148°, while a flat maximum in the tensile strength was found with 6 per cent. of sulphur, no well-defined maximum at all was found with 5 per cent. With the last-mentioned percentage the tensile strength reached its highest value at a combined-sulphur figure of nearly 4.5 per cent., and oscillated in the same neighbourhood over a wide range of curing periods. Further, the length at break and the position of the stress-strain curve for 6 per

cent. or less of sulphur changed in a manner different from that, found with higher percentages of sulphur, which may be considered normal, and which has been described earlier. As the period of cure was continued beyond that at which the highest value for the tensile strength is reached, instead of the vulcanizate showing a continually diminishing length at break, and a continually lower position of the stress-strain curve, indicating that the rubber was gradually becoming brittle, the length at break began to increase, and the stress-strain curve began to move backwards, *i. e.* upwards.

This state of affairs is represented by the upward and backward bend of the curve showing the breaking-points for the 6 per cent. mix (Fig. 30). The 5 per cent. mixes show the effect more strikingly, the loops which the corresponding curves indicate being much narrower. In Fig. 30 are also shown in part the breaking-points for Sample 452 (Table XCVII) cured with 7.5 per cent. of sulphur from a point near that giving the maximum tensile strength (75 mins., giving  $P_B$  1.33,  $L_B$  1011) up to a point at which the vulcanizate was brittle (240 mins., giving  $P_B$  0.15,  $L_B$  427). As would be anticipated from results for the thirteen samples mentioned earlier, the curve representing the breaking-points does not show a loop.

TABLE XCVII  
Sample 452 cured at 148°

Period of cure (min.)	90	105	120	135	150	180	240
With 6 per cent. sulphur	$P_B$ .	1.31	1.35	1.33	1.26	1.19	1.07
	$L_B$ .	1088	1046	1028	1001	992	1015
	$L_{1.20}$ .	1071	1024	1009	992	993	1001
	$S$ .	4.17	—	5.13	5.47	5.78	5.86
With 5 per cent. sulphur	$P_B$ .	1.19	1.22	1.35	1.27	1.31	1.20
	$L_B$ .	1157	1124	1124	1104	1105	1110
	$L_{1.20}$ .	1159	1122	1101	1095	1089	1109
	$S$ .	3.83	—	4.41	—	4.77	—
Period of cure (min.)	75	90	105	120	150	240	
With 7.5 per cent. sulphur (Optimum cure = ca. 80 min.)	$P_B$ .	1.33	1.31	1.15	0.71	0.17	0.15
	$L_B$ .	1011	977	906	795	472	427
	$L_{1.20}$ .	991	960	913	870	—	—
	$S$ .	—	—	—	—	—	—

$S$  = Percentage of combined sulphur (calculated on the mix).  
 $L_{1.20}$ , *i. e.*, the length corresponding to a load of 1.20 kg./mm<sup>2</sup>, indicates the position of the stress-strain curve.

The following figure includes the breaking-points for two additional samples, not included in Table XCVII.

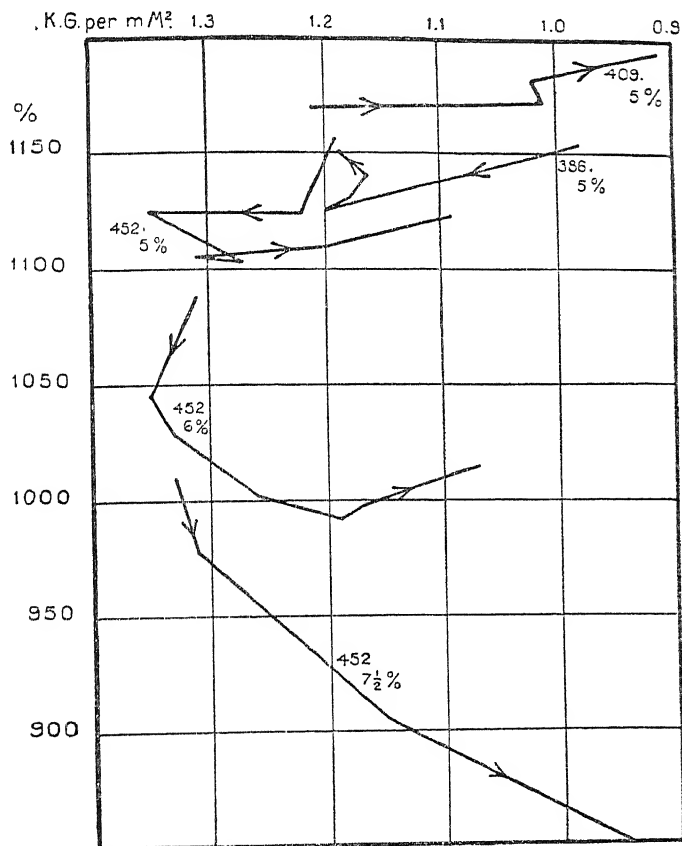


FIG. 30.—Curves of the breaking-points for rubber-sulphur mixes containing 7.5, 6 and 5 per cent. of sulphur (see Table XCVII).

In the case of the mixes containing 6 per cent. and 5 per cent. of sulphur, it appears that the abnormal movement of the breaking figures begins when almost all the sulphur has entered into combination. (In the case of the mix containing 7.5 per cent. of sulphur, complete combination of sulphur would fall in the region where the rubber is quite brittle and no stress-strain curves can be obtained.)

Schidrowitz and Goldsbrough<sup>1</sup> have applied the term "rever-

<sup>1</sup> *I.R.J.*, 1919, 57, 269.

sion" to the backward movement of the stress-strain curves, such as that noted above in relation to mixes containing 6 per cent. or less of sulphur. They state that in their own experience they have observed such reversion on continued heating of a mix containing rubber, an inert inorganic material and sulphur in the proportions 70 : 27 : 3. They point out that such reversion is to be considered as displaying the effects on the vulcanizate of heating *per se* as opposed to the effects of heating in producing vulcanization.

Concerning the significance, in regard to the question of the nature of vulcanization, of the occurrence of "reversion" on continuing to heat a mixture of rubber and sulphur after substantially all the sulphur has entered into combination, Schidrowitz and Goldsbrough write as follows: "These phenomena are in accord with the view that in the process of vulcanization two main factors are operative, namely: (1) a process of integration, pectization or 'firming up,' which consists in (or goes hand-in-hand with) the chemical process of combination of sulphur with the rubber, and (2) a disintegrating or degradation process due to the heat effect as such. When further combination with sulphur is no longer possible, the heat effect becomes apparent and causes reversion and degradation."

These authors suggest that a study of "reversion" of the stress-strain curve should be of practical value in permitting a rapid and accurate estimation of over-heating, as opposed to over-curing, in, for instance, the manufacture of goods cured with minimal proportions of sulphur.

De Vries and Hellendoorn examined also a rubber-sulphur mix containing only 3 per cent. of sulphur. The vulcanizates obtained were at all cures too soft to reach the breaking-point before a length of 1225 per cent., which is the maximum which the Schopper machine allows. But it was clear that the mix showed even more markedly the "abnormal" phenomena which had been found for the 5 per cent. mixes. Instead of becoming continually harder with increasing period of cure, the material began, when the cure was continued beyond the period giving the highest tensile product and corresponding to complete combination of the sulphur, to become softer, and the stress-strain curve showed increasing reversion. In the following table the reversion is indicated by the smaller load required to produce a fixed extension, namely, a length of 1225 per cent.

TABLE XCVIII

*Sample 452 cured in mix with 3 per cent. sulphur, at 148°*

Period of cure (min.)	76	90	120	135	150	180	240
P <sub>1225</sub>	0.31	0.375	0.40	0.395	0.38	0.37	0.265
Combined S (on mix)	—	2.59	2.81	3.01	—	—	3.05

An important point, regarding the exact course of the stress-strain curves, which was observed in connection with the investigation of de Vries and Hellendoorn was that, unless reversion had occurred, for mixtures of rubber and sulphur with different sulphur-contents, stress-strain curves showing the same position, as determined by taking the length at a given load, appeared to have the same form, and had the same inclination over the flat portion, *i. e.* the same "slope" (cf. p. 352).

*Other factors influencing the sharpness of the maximum.*—Naturally the temperature of vulcanization will influence the sharpness with which a maximum occurs in the tensile strength, in the sense that the maximum will be sharper in a series of cures made, with given intervals, at a higher temperature than in a series, with the same intervals, at a lower temperature. A comparison of cures at 147.1° with cures at 138.1°, shown in Table XCI, will provide an example of the influence of temperature on the sharpness of the maximum.

Another factor relevant to the question of the sharpness of the maximum is the character of the raw rubber itself—whether slow- or rapid-curing. That a rapid-curing rubber will, in a given mix subjected to progressive cures at a given temperature, show a sharper tensile maximum than a slow-curing rubber in similar circumstances may be gathered from an inspection of the data shown in Table LXXXVIII. Here the rapid-curing sample ("slab" rubber) shows its maximal tensile strength, 1.45 kg./mm.<sup>2</sup>, at a cure of 1.5 hours, and has already collapsed, to 0.53 kg./mm.<sup>2</sup>, with a further 0.25 hours' curing. The tensile strength of the slow-curing samples (sheet and crêpe) do not show a similar collapse in their tensile strength until the period of cure giving the maximal tensile strength has been increased by 0.75 hours.

In results obtained by Eaton and Grantham<sup>1</sup> when comparing a sample of rapid-curing (slab) rubber and a sample of slow-

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 1048.

curing (crêpe) rubber, cured for increasing periods at 140° with 10, 9.1, 7 and 4.8 per cent. of sulphur, there may be read the influence on the course of the tensile strength of all the three factors already mentioned, namely: (a) percentage of sulphur, (b) character of the rubber, (c) temperature of vulcanization. In this comparison each mix was subjected to either five or six cures, except C, which had eight cures, for the periods indicated in Fig. 31. The tensile strength at each cure is shown in the figure. In all cases the length at break fell continuously with increasing cure, except in the case of C (slab with 4.8 per cent. sulphur), where a slight reversion was indicated, the length for the four-hour cure being 1140 and for the five-hour cure 1150.

Comparing the mixes containing the rapid-curing rubber among themselves, it will be observed that C, in which the percentage of sulphur is only 4.8, gives only a flat maximum, whereas the mixes with larger proportions of sulphur, *i. e.* A, B, D, give sharp maxima. Comparing the mixes containing slow-curing rubber among themselves, it will be observed that, within the limits of the experiment, only the one containing 10 per cent. of sulphur shows any maximum at all.

Comparing the mixes of rapid-curing rubber with the corresponding mixes of slow-curing rubber, it will be observed that, in the case of the pair A and E, A gives a sharper maximum than E, and that, in the case of the other three pairs, the rapid-curing rubber gives a maximum, whereas the slow-curing rubber has not arrived at a maximum in the limits of the experiments, and, too, shows a much less sharply inclined curve.

The influence of temperature, although not shown in the results considered alone, may be gathered from a comparison of the results for the crêpe rubber with the results, already noted, obtained by de Vries for crêpe cured with 10 and 7.5 per cent. of sulphur at a temperature 8° higher. At 148° crêpe cured with 10 and with 7.5 per cent. of sulphur showed sharper maxima for tensile strength than did the mixes, E, H and F, cured at 140°.

It will be observed from the above results that, even though no sharp maximum may be obtained with a small proportion of sulphur in the case of ordinary crêpe or sheet rubber, it may be obtained with such a proportion of sulphur in the case of a rapid-curing rubber. The effect of the addition to ordinary sheet or crêpe of artificial accelerators is, it appears, the same

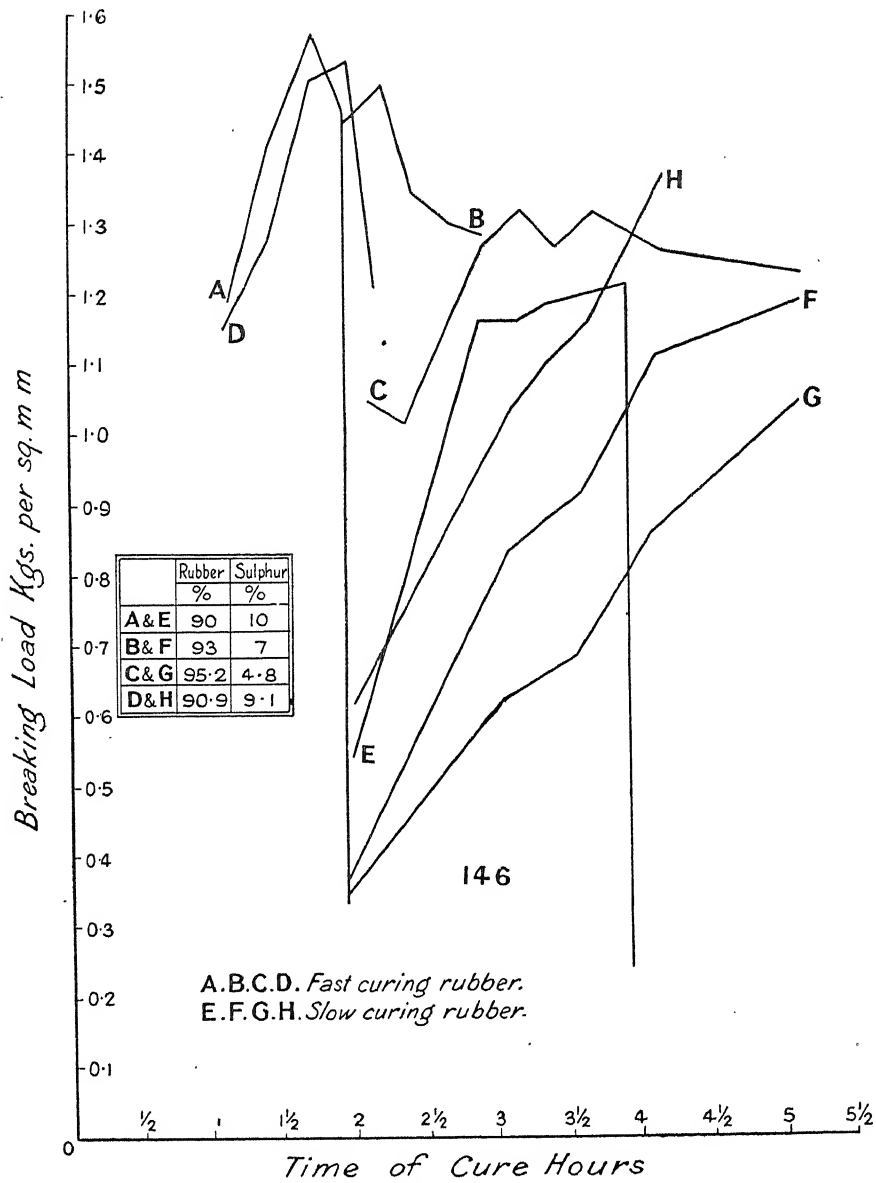


FIG. 31.



as natural rapidity of cure in leading to the occurrence of a sharp maximum in the tensile properties.<sup>1</sup>

*Conclusion.*—In view of the preceding discussion it may be said, by way of summary, that any factor which increases the rapidity of vulcanization, such as a higher temperature, a higher proportion of sulphur, the presence of natural or artificial accelerators, will tend to accentuate the sharpness with which a maximum occurs in the vulcanizates obtained by progressive curing.

Further: in the conclusions which have emerged from the preceding discussion may be seen a justification of the choice, for the purpose of comparing different samples of rubber in a rubber-sulphur mix, of proportions of sulphur so large, when compared with the proportions generally employed in technical mixes, as 10 per cent. (with a vulcanizing temperature of 140°—Eaton), 7.5 per cent. (with a vulcanizing temperature of 148°—the Delft Institute, de Vries) and 8 parts per 100 of rubber (with a vulcanizing temperature of 141°—Schidrowitz). For a discussion of the relation between the behaviour of simple rubber-sulphur mixes containing proportions of sulphur such as those just mentioned, and the kind of mixes employed technically for the manufacture of "mechanical" rubber goods, see Chap. XVI.

#### PROPERTIES SHOWING NO MAXIMUM

Mention may be made of a number of properties which have been examined in their relation to progressive curing, but which, unlike tensile strength, change continuously without showing a maximum. Clearly, tests referring to such properties, while they may be of value in testing the suitability of given vulcanized rubbers to fulfil specific technical purposes, cannot have the value that the tensile strength has for the comparative examination of raw rubber samples on a general basis. Tests which do not show any maximum are, in general, those which may, in some respects, be regarded as merely registering the increasing hardness of the vulcanizate with increasing cure. The values for the elongation at break (after the initial period of "pre-vulcanization") considered by itself, for "rebound," for "rupture after repeated stretching," and possibly for "set"—all show a continual decline with progressive curing.

<sup>1</sup> Conclusion based on unpublished experiments by the author and O. J. Walker.

"Rebound" has been studied rather extensively by the Delft Institute, by means of the apparatus described by Breuil,<sup>1</sup> and known as an "elastometer," in which the rebound of a steel ball falling from a height of 25 cm. on to the rubber sample is read, and by means of the "shock test apparatus," devised by van Iterson,<sup>2</sup> in which the rebound of a pendulum from the rubber sample is charted on a rotating drum. It was found that the rebound diminished continually with advancing cure. From the following table,<sup>3</sup> showing the results of progressive cures at 148° of a mix rubber 92.5 : sulphur 7.5, it may be seen that, while the tensile strength shows a maximum, the rebound falls continually.

 TABLE XCIX <sup>4</sup>

Time of cure (min.)	0	10	20	30	60	90	120	180	240	360	480
Pb . . . .	0.059	0.039	0.095	0.175	0.670	0.90	0.80	0.20	0.22	0.14	0.16
Lb . . . .	82	682	754	887	940	882	668	366	424	313	384
Rebound (cm.)	16.9	15.2	15.0	14.7	14.0	13.7	12.7	9.8	7.9	6.9	6.4
Set (mm. measured 24 hrs. after break)	18	16	11	13	10	10	9	6	5	6	6

It was found that the rebound fell more quickly in the region of over-curing than before. It will be observed that in the above series the set also diminished continuously with advancing cure. A similar result regarding set was also found in another series of progressive cures which were examined.<sup>5</sup> It should be noted, however, that the set recorded appears to be that remaining after extension to the breaking-point; and, hence, that the more advanced cures would be subjected to a smaller strain than the less advanced ones. It would not, then, appear to be legitimate to conclude from these results that the set as determined in the more usual way, *i. e.* after extension to a fixed point short of the point of rupture, will fall continually with progressive curing.

More numerous results given by Eaton<sup>6</sup> for the set after extension to a point short of rupture, however, do in fact agree

<sup>1</sup> *Le Caoutchouc*, 1908, 5, 2186.

<sup>2</sup> *Meded. Delft*, 1916, p. 96; *Delft Communics.*, p. 172.

<sup>3</sup> Fol. and van Heurn, *Meded. Delft*, 1916, p. 338; *Delft Communics.*, p. 218.

<sup>4</sup> The vulcanization coefficients corresponding to the cures in this table are given in Table LXXXVII.

<sup>5</sup> Fol. and van Heurn, *Meded. Delft*, 1916, p. 343; *Delft Communics.*, p. 189.

<sup>6</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 381 *et seq.*

with the results of the tests described above in finding the set to diminish continuously with progressive curing.<sup>1</sup> Ring test pieces were held at a length of 500 per cent. for twenty-four hours; and the set was measured after a recovery period of six hours. The fixed extension mentioned was such that samples which, as judged by the optimum curve, were about a quarter of an hour over-cured almost invariably broke during the twenty-four hour period. The length of the rings before and after the experiment was measured under a small, fixed load, intended to straighten the ring, on the Schopper ring-measuring instrument.

The following table shows the set for a sample of rapid-curing rubber (matured coagulum), A, and for a sample of slow-curing rubber (latex crêpe), B, cured over a range of times. The breaking figures are represented in the table by the tensile product,  $P_B \times L_B$ . The optimum cure is indicated by an asterisk.

TABLE C

Time of cure (hrs.)	0.25	0.5	0.75	1	1.25	1.5	1.75	2	2.25
A (Set (per cent.) . $P_B \times L_B/100$ .	37.2 4.66	17.0 8.40	9.6 10.19	5.3 11.81	3.1 12.46	3.1* 14.89*	1.0 14.16	Broke 11.42	— 3.77
B (Set (per cent.) . $P_B \times L_B/100$ .	—	—	—	50.0 3.98	31.9 5.63	26.6 6.41	19.2 5.38	14.9 7.91	10.6 6.31

Time of cure (hrs.)	2.5	2.75	3	3.25	3.5	3.75	4	4.25
B (Set (per cent.) . $P_B \times L_B/100$ .	8.5 8.15	6.4 10.50	4.2 11.50	4.2* 12.25	3.1 12.23	—	3.1 12.70	2.1 10.41

Eaton concludes that the set is not so sensitive to changes in the state of cure as either the stress-strain curve or the tensile strength. He found, *e. g.*, that rings corresponding to cures differing by half-an-hour frequently gave identical results for set. He found, further, from an examination of the set at the

<sup>1</sup> Attention should, however, be called to Kratz and Flower's data, shown in Table CXVIII, for set in the case of a mix containing zinc oxide. In this case the amount of set did not decrease continuously with increasing cure. Possibly this result may be due to the "mineralization" of the rubber. It is not stated under what conditions the set was measured, but presumably it was after only a brief interval for recovery. The determination of set under such a condition is open to considerable experimental error. The general character of the figures does not, however, suggest that their course is noticeably influenced by experimental error.

optimum point, as decided by his standard curve or by the maximal value of the tensile product, that the value for set at this point was not constant. Data for seventy-four samples, which represent a selection of the samples examined, are tabulated. De Vries and Hellendoorn have found set to be directly related to the inclination of the flat part of the stress-strain curve (see p. 450).

Memmler<sup>1</sup> records some results obtained on a machine designed by Martens by which a number of rings are stretched to a small extension and allowed to retract repeatedly until they break; the recording mechanism attached to each ring stopping automatically when the ring breaks. Some of the results are shown in the following table.

TABLE CI

*The material in each case consisted of Para rubber with 10 per cent. of sulphur*

	Greatest elongation (per cent.) observed in each of three tests.			Mean number of extensions and re- tractions before breaking in three parallel tests.
Material, 25 per cent. under-cured.	87	87	87	156,050
„ fully cured . . . . .	86	86	86	130,000
„ 25 per cent. over-cured .	86	86	86	96,310
„ 50 per cent. over-cured .	86	86	86	60,980

<sup>1</sup> *Rubber Industry*, 1911, p. 357.

## CHAPTER XIV

### COMPARISON OF RAW RUBBER SAMPLES

#### STATE OF CURE AND RATE OF CURE

IN the first attempts made to compare <sup>1</sup> samples of rubber by means of vulcanization tests the different samples were usually vulcanized under the same conditions, *i. e.* in a mix of the same composition, at the same temperature, and for the same period of time; and were then subjected to tensile tests. It became clear, however, that, though at first sight a comparison of the effect on two samples of rubber of the same treatment might appear to offer a reasonable and fair method of judging the relative values of the samples, it was not, in fact, satisfactory. It became clear that it was necessary to take into account the "state of cure" of the samples. By the term "state of cure" it is intended to indicate the position of a cure in a series of progressive cures. It became clear that for a satisfactory comparison of two samples of rubber the *series* of cures which the samples would yield must be taken into consideration, either by the laborious procedure of actually making the series, or, better, by some procedure, which, while having reference to the conception of a series of cures, would be, in its experimental aspect, briefer.

As the result of one cure alone is an insufficient guide to the character of the series of cures to which it belongs, it is impossible to make a satisfactory comparison of rubber samples by subjecting them to one (and the same) cure. Conclusions drawn from comparisons based on the results of a single cure have not infrequently led to rather serious errors. The results shown in Table LXXXVIII may be examined for an illustration in this connection. If the three samples of rubber here in question had been compared solely on the basis of the results shown

<sup>1</sup> In the present and in the succeeding chapter the comparison of rubber samples on general lines, when vulcanized with sulphur only, is in question. Regarding the comparison of samples of rubber for specific technical purposes, see Chap. XVI.

after curing all the samples with the same proportion of sulphur, at the same temperature, and for the same period of time, two hours, an entirely incorrect judgment might have been made as to the relative quality of the samples; particularly when it is considered that at the time when the comparison of rubbers on such a basis was attempted, the character of the series of progressive cures given by different types of rubber had not been investigated closely.

It soon became clear that, although it was convenient to employ a constant proportion of sulphur and a constant temperature for the comparison of rubber samples, it was not satisfactory to employ a fixed period of vulcanization. It was clear, for example, that, of two rubbers cured for a given period, one would perhaps have yielded a better product with a longer period, and the other perhaps with a shorter period. It appeared more satisfactory to make the comparison of rubbers have reference to the *best* tensile results which each could be made to yield by adjusting the period of vulcanization.<sup>1</sup> Without prejudging the question, to be discussed later, as to how exactly the best result for a given rubber may be defined, the term

<sup>1</sup> *The Delft Institute's method.*—Reference should be made here to the method of comparison employed by the Rubber Institute at Delft. A fixed period of vulcanization, viz. 1.5 hours, was adopted; the temperature of vulcanization being 3.5 atmospheres steam pressure (148°), and the percentage of sulphur in the rubber-sulphur mix being 7.5. The results given under these fixed conditions by several large collections of rubber samples have been treated by the Institute in a statistical manner (*vide*, particularly, van Rossem, *Bijdrage tot de kennis van het Vulcanisatieproces*, Amsterdam, 1916). This method of treatment has educed from the data some interesting results, a number of which are given at various points in the present volume, with reference, particularly, to the relation between various analytical quantities and the rate of vulcanization. The statistical treatment also enables the "normality" of a sample of rubber to be judged. It is obviously possible, by treating statistically the data for a random collection of samples of rubber of a given type (say, smoked sheet), to establish, for example, the "normal deviation" in the position of the stress-strain curve for a given coefficient of vulcanization.

A statistical mode of treating vulcanization data obtained under fixed curing conditions undoubtedly could be made useful—for example, in comparing the rates of cure of rubbers of a given type. But, as a method of general evaluation, it does not commend itself. Even when subjected to the careful statistical treatment that has been employed by the Delft Institute, the results of a single cure under fixed curing conditions do not allow of a complete judgment of the quality of different samples of rubber, even when the samples are of the same type, and less so when they are of different types. It may be observed, as one of the fundamental reasons for this, that the tensile results obtained under given curing conditions show the influence of two factors, which it is impossible to distinguish from the results of only one cure, viz. the rate of cure and the innate tensile quality of the sample. Probably in most cases the former influence is predominant.

"optimum cure" may be adopted to designate the cure which gives such results.

It is clear, from what has been said in the preceding chapter, that there is a gradation of properties—say, *e. g.*, of tensile strength—in a series of progressive cures on any one sample of rubber, and that, when comparing the series given by different samples of rubber, the same relative point in the gradation is reached by different samples at different rates. Thus, referring again to Table LXXXVIII (p. 317), the slab sample gives its maximum breaking stress at a cure of 1.5 hours, the sheet sample at a cure of 2.5 hours, and the crêpe sample at a cure of 3 hours; that is to say, the samples differ in what may be called their *rate of cure*. The conceptions of rate of cure and of state of cure are fundamental to the development of a satisfactory method of comparing samples of rubber by means of vulcanization tests. These conceptions have, as will be clear from what has gone before, either explicit or implicit reference to series of progressive cures.

#### THE BREAKING FIGURES AND THE STRESS-STRAIN CURVE AS INDEXES TO THE STATE OF CURE

Progressive curing, considered in relation to the tensile properties of the vulcanizates, has, at all events until quite recent years, been considered most generally with reference to the breaking-point only. And in the vulcanization testing employed in rubber works the state of cure in regard to tensile properties is, in the majority of cases, still judged by the breaking figures—except in so far as hand-pulling, biting and other such means are relied upon. During very recent years the study of progressive curing has been begun in relation not only to the breaking of the vulcanizate, which represents merely the end-point of the stress-strain curve, but also in relation to the whole stress-strain curve; and it has become apparent that, for the conduct of vulcanization tests in rubber-sulphur mixes, consideration of the whole stress-strain curve, and not merely of its end-point, is demanded.

Apart from the fact that, to attempt to judge the state of cure from breaking figures alone involves neglecting consideration of the stress-strain relations throughout the course of the stretching, which, it now appears, is full of significance, there is to be taken into account the fact that the experimental determination

of breaking figures is affected by a probable error of such a magnitude that breaking figures as determined under ordinary testing conditions may be seriously inaccurate. It has been the experience of all who have conducted tensile tests on rubber that there is a very considerable element of fortuity in the numerical values obtained for the breaking-point of a given rubber. While the effect of such fortuity may to a large extent be neutralized by taking the breaking figures for a given vulcanizate as the mean of a fair number of determinations on separate test pieces, in order to neutralize it so completely as to get exact breaking figures, the number of specimens which must be tested is large—much larger, as may be judged from an examination of the data, regarding the number of rings tested and the corresponding probable errors, in Tables LXXXIX and XCIV, than it would be practicable to test, except in special circumstances.

Data showing the extent of fortuity which ordinarily affects tensile tests made with rings on the Schopper machine have been published by the Delft Institute,<sup>1</sup> and by Eaton,<sup>2</sup> in addition to the data of de Vries and Hellendoorn, some of which has been given in the two tables just mentioned. The extent may be indicated by a reference to the data summarized in Table LXXX (p. 292). In four sets—each set from the same test slab—of 8-9 rings, from which the mean figures shown in the table were obtained, the figures for the breaking stress ranged—following the order of the table—from 0.98 to 1.26, from 1.12 to 1.33, from 1.08 to 1.35, from 1.07 to 1.35; the range was roughly 25 per cent. In some further tests on vulcanization technique<sup>3</sup> it was found that, in a case where sixteen test pieces of each sample were examined, the "probable error" for a mean  $P_B$  of 0.84 was  $\pm 0.0234$ , and for a mean  $L_B$  of 926.2 was  $\pm 10$ . (In this case four pieces were vulcanized at a time; and half the pieces were tested by one operator and half by another.)

But, although a number of different test pieces from the same vulcanizate may be found to show such a considerable degree of fortuity in their breaking-points, they will not be found to show any such fortuity in the course of their stress-strain curves; the latter will be found to be practically coincident. The curves for some specimens will break off sooner or will break off later than the curves for some other specimens, but up to its end-

<sup>1</sup> *Meded. Delft*, 1916, p. 89; *Delft Communics.*, p. 153.

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 36.

<sup>3</sup> *Delft Communics.*, p. 163.



point every curve will be practically coincident with every other curve. That is to say, while the exact end-point of the stress-strain curve at a given state of cure is accidental, the general course of the curve is fixed. The following example (Table CII) from Eaton's work will show this. In the example quoted,  $P_B$  in one case ranges, for eight test pieces, from 0.78 to 1.09—a range of 40 per cent.<sup>1</sup> calculated on the lower figure; and in the other case, for six test pieces, from 1.14 to 1.34—a range of 17 per cent.; yet the stress-strain curves, shown in Fig. 32, are in each case almost identical in their course.

TABLE CII

*Sample cured in a mould with 10 per cent. of sulphur (calculated on the mix) for 2 hours. Eight rings cut from a single test slab.*

No. of ring	1	2	3	4	5	6	7	8
$P_B$	1.08	1.01	0.92	0.98	0.89	1.09	0.78	0.82
$L_B$	1089	1074	1060	1066	1089	1074	1031	1029

*Sample cured under same conditions as above for 2.5 hours. Six rings cut from a single test slab.*

No. of ring	1	2	3	4	5	6
$P_B$	1.15	1.27	1.24	1.33	1.34	1.14
$L_B$	1013	1030	1025	1035	1039	1011

The end-points of the curve for each ring are indicated by a corresponding number in the figure.

No similar data for straight (dumb-bell) test pieces have been published. As has already been mentioned, such test pieces do not lend themselves to exact measurement of the elongation, particularly throughout the course of the stretching. The experience of the present writer is, however, to the effect that, with dumb-bell test pieces, as with ring test pieces, while, for a given state of cure, the actual breaking figures are subject to considerable accidental errors, the course of the stress-strain curve is fixed. In order to secure the stress-strain curves with test pieces of the shape in question, the loading was conducted at a fixed, slow rate, with halts at definite intervals for making measurements of the distance between two gauge marks. (With several operators it is possible, with straight test pieces, to get approximate readings

<sup>1</sup> This is perhaps somewhat of an extreme, but not a rare range. It may be mentioned that the rubber is not over-cured, but, rather, under-cured. (As noticed later, the magnitude of the accidental errors in the breaking figures tend to be greater in over-cured than in under-cured samples.)

of stress and strain from which a stress-strain curve can be plotted.)

The cause of the accidental errors in the breaking figures of rubber specimens is in part obscure. In some cases a clearly exceptional break can be referred to some obvious flaw, such as a particle of sand or a gas bubble. In such cases the results for the test piece in question are reasonably rejected. But the normal fluctuations in the breaking figures cannot be referred to such visible flaws. Doubtless slight jars in the stretching when

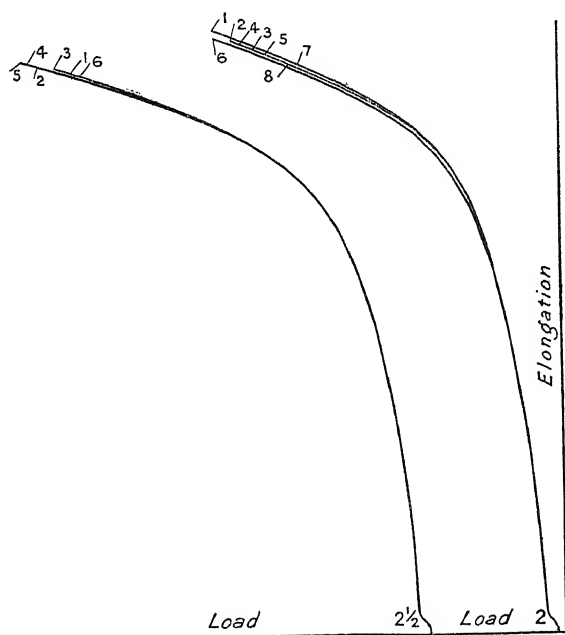


FIG. 32.

the specimen is near its breaking-point constitute one factor in the production of normal fluctuation. It may be remarked that over-cured samples and most technical mixes, both of which approach nearer to brittleness than a properly cured rubber-sulphur vulcanizate, are subject to more considerable accidental errors than the latter.

#### THE OPTIMUM CURE

It is, obviously, possible to determine the optimum cure of a given sample, defined with the breaking figures in view, for the

purpose of comparison with other samples, by subjecting the sample to a series of cures and determining the breaking figures given at each cure. But in order to secure exact breaking figures, it is, as the preceding section has shown, necessary to test a large number of test pieces. Hence, to select with certainty the optimum cure from the breaking figures alone would be a very laborious proceeding, which could be undertaken only in very special cases, as may be judged from a glance at Tables LXXXIX and XCV. The stress-strain curves enable the optimum cure to be selected much more easily, and, at all events unless a large number of test pieces is examined, with much greater certainty than do the mere breaking figures. (And, further, they give additional valuable information which cannot be derived from the breaking figures.)

While the breaking figures for a given test piece are an uncertain index to the state of cure, the stress-strain curve is a precise index to it. In the ordinary case, where the number of test pieces examined is few, or even only one, the breaking figures may show considerable irregularities in a series of progressive cures, but the stress-strain curves will move in a perfectly regular fashion. A stress-strain curve lower on the paper, strains being taken as ordinates, is indicative of a more advanced state of cure than a curve higher on the paper; and, speaking roughly, providing that the composition of the mix is the same, this is so whether the curves have reference to the same or to different rubbers.

The state of cure at which it is desired to compare different samples of raw rubber is the optimum state for each sample. From what has been said it will be clear that, considering a series of progressive states of cure of a given sample, the optimum state can be expressed more precisely and conveniently by means of the position of the stress-strain curve corresponding to it than by means of the breaking figures. As to how far it would be true to say that the curves representing the optimum cures of different samples of rubber are coincident will be discussed in the section on the "slope" of the stress-strain curve (p. 356). But it may be said that for a first approximation a single curve may be adopted as representing the optimum cure for all samples. Eaton selected a "standard curve"—indicated in Fig. 26—with which to compare rubbers vulcanized in a given mix at a given temperature. The curve was an average one, selected from the curves given by a large number of samples of rubber

of widely differing rates of cure; the optimum cure being taken as the cure at which the product ( $P_B \times L_B$ ) was maximal (cf. succeeding section).

Eaton<sup>1</sup> reports for each sample of a collection of several hundred samples both the time of cure giving the Optimum Cure, considered as that cure corresponding to his standard curve, and the time of cure giving the Optimum Cure, considered as that cure showing, from tests on two test rings only, the maximal value of the product ( $P_B \times L_B$ ). And, it may be remarked, the two times seldom differ by more than a quarter of an hour. Eaton regards differences in the time of the Optimum Cure, considered with reference to the two above-mentioned criteria, as attributable rather to errors in the breaking figures than from inconsistencies arising from the use of a single standard curve. (Cf., however, the section on the "slope" of the stress-strain curve, p. 353 *et seq.*)

De Vries has adopted as a standard the curve passing through the point P, 1.30 kg./mm.<sup>2</sup>, L, 990 per cent. The cure represented by this curve is in the case of a majority of samples of *Hevea* rubber identical with or close to the cure giving the maximal tensile strength.<sup>2</sup>

The rates of cure of different samples of rubber, compared by vulcanizing them in a given mix at a given temperature, are to be regarded as the rates at which they arrive at their optimum cures. Rate of cure is most conveniently expressed by giving the time required to reach the optimum cure, *i. e.* by giving the inverse of the rate. The use of the stress-strain curves allow the relative rates of cure of different samples of rubber to be rendered with a rapidity and precision of which the breaking figures do not allow. And it is largely due to the use of the curves that such satisfactory progress has recently been made in the investigation of variation in plantation rubber, and of the influence of various factors involved in the preparation of rubber from latex on the quality of the product.

The fact that of two rubbers cured for the same period of times—take, for example, the slab and the sheet in Fig. 24 at a 1.5-hour cure—one gives a curve lying higher on the paper than the other shows at once that the rubber in question is in a less advanced state of cure, and hence is a slower-curing rubber than the other. Further, the position of the curves relative

<sup>1</sup> Dept. Agric. F.M.S. Bull., No. 27, 1918, p. 398.

<sup>2</sup> De Vries and Hellendoorn, *Archief*, 1918, 2, 769.

to a standard curve at once indicates very approximately the rates of cure of the samples. And a little experience will suggest to what extent the period of cure of each of the samples requires to be adjusted in order to bring the curve into the standard position. Hence, if use is made of the stress-strain curves, it is, for the purpose of comparing rubber samples, generally necessary to perform only two cures: a preliminary one and a final (adjusted) one.<sup>1</sup> Where use is made only of the breaking figures, it is, of course, possible, with some experience, to estimate the adjustment necessary in the cure of a sample necessary to give the optimum cure, but not by any means with such precision or rapidity as where use is made of the stress-strain curves.

A standard curve represents the state of cure to which it is desired to bring a sample in a precise manner, so that it can be said at once from the position of the curve whether the standard cure has or has not been made. Where the standard state of cure is defined with regard only to the breaking figures, it can be said with certainty whether that cure has or has not been made only by much labour—by making cures on either side of the supposed state and by examining a large number of test pieces.

*Maximal breaking figures.*—Whether that cure which gives the best breaking figures is, in fact, the best or optimum cure of the series will be discussed later (p. 380). It clearly, however, forms a definite point of reference in a series of cures, and, as such, may be regarded, at all events provisionally, as the optimum cure. There has been a little difference of view as to whether the optimum cure, regarded in this sense, is most suitably selected with reference to the tensile strength alone ( $P_B$  max.), or with regard to both the tensile strength and the length at break. Eaton, as already mentioned, takes the optimum cure (here considered in regard to the breaking figures only) as the cure giving the maximum product,  $(P_B \times L_B)$  max. The product  $P_B \times L_B$  is called by Stevens the "tensile product."

Owing to the fact that, in a series of progressive cures, the change, in the neighbourhood of the optimum cure, is much slower in regard to breaking length than in regard to tensile strength, the position of the maximal product seldom differs much from the position of the maximal tensile strength. This may be seen, for example, in the following table, in which are

<sup>1</sup> Occasionally, of course, the adjustment necessary will be slightly mis-estimated, and a further adjustment may be called for.

summarized the results obtained by the Delft Institute<sup>1</sup> from cures, all made under the same conditions, of 341 samples of latex crêpe.

TABLE CIII

Vulcn. coeff. (indicating state of cure)	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
Most probable $P_B$	0.643	0.776	0.91	1.04	1.177	1.284	1.382	1.373	1.155
$L_B$	965	950	930	915	910	895	890	835	800
Product $(P_B \times L_B)/100$	6.20	7.46	8.42	9.52	10.71	11.49	12.30	11.74	9.24

The values for the tensile product run parallel with those for the tensile strength. The Delft Institute concludes that "the product figure as applied by Eaton and Grantham teaches nothing more than the tensile strength considered by itself, hence its use should be rejected." It should, however, be remarked that the parallelism as seen in the above table results in part from the fact that the data are treated statistically in groups. While it is undoubtedly true that the position of maximal tensile strength is usually coincident with the position of maximal tensile product, and while for most purposes either means of marking the highest breaking-point may be adopted without serious influence on the results, it is not invariably found to be exactly coincident; and, as Eaton points out, the tensile product may be considered as rendering the breaking-point in a more rational manner than the tensile strength alone, since the latter gives the breaking stress referred to the original cross-section, whereas the former, on the assumption that the volume of the rubber remains unchanged by stretching,<sup>2</sup> gives the breaking stress referred to the actual cross-section at the breaking-point.

*"Slope" of the stress-strain curve and the Optimum Curve.*—The stress-strain curves forming a series representing progressive cures of a given mix, while varying in inclination over the steep portion, are, as may be gathered from an inspection of the various series of curves shown in the preceding chapter, parallel over the flat portion of the curves; that is to say, the inclination of the flat portion of the stress-strain curve is independent of the state of cure. On account of the fact that this portion of the curve is *typical* of the curves referring to a given mix,

<sup>1</sup> Delft Communics., p. 159.

<sup>2</sup> Cf., however, Chap. XXI, particularly Schippel's results on the increase in volume of mineralized rubbers on stretching.

Schidrowitz has, with some justice, employed the term "type" to denote its inclination. It seems, however, preferable, on the whole, in order to avoid possible confusion, to speak simply of the "slope" of the flat portion of the curve.

The constancy of the slope for a given rubber cured in a given mix is not, according to Schidrowitz,<sup>1</sup> affected by the extent of working to which the rubber is subjected on the mixing rolls; and it is not, according to de Vries and Hellendoorn,<sup>2</sup> affected by changes in the percentage of sulphur used.

Schidrowitz is responsible for drawing attention to the significance of the slope of the stress-strain curve.<sup>3</sup> He also pointed out that the curves for different samples of rubber, vulcanized with the same proportion of sulphur and at the same temperature, may differ in slope. The differences are not large, but are, not improbably, of considerable significance. That the slope of the stress-strain curve may vary with different rubber samples has been confirmed by Whitby<sup>4</sup> and by de Vries.<sup>5</sup> Eaton and Grantham<sup>6</sup> concluded that there were no differences in slope in the curves for different samples. Whitby<sup>7</sup> pointed out that the explanation of Eaton and Grantham's failure to find any differences of slope in the collection of samples in question, probably lay partly in the circumstance that all the samples "were coagulated in a similar manner from the same trees," as he found that samples prepared from any one area were likely to be uniform in their slope, but that samples from different areas might differ in their slope, and partly in the circumstance that the scale on which the stress-strain curves are drawn by the Schopper machine is not well suited to bringing out differences in slope. In order to examine the slope of the stress-curve conveniently, it is desirable that the scale on which the stresses are plotted should bear a higher ratio to the scale on which the strains are plotted than is the case with the autographic apparatus on the Schopper machine as ordinarily employed.<sup>8</sup>

<sup>1</sup> "In overworking within reasonable limits, not working the rubber in such a way as to reduce it to a jelly, but giving it an extra half-hour or quarter of an hour on the mill, it has been found that rate of cure but not type (slope) is affected."—*Rubber Industry*, 1914, p. 227.

<sup>2</sup> *Archief*, 1918, 2, 769.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1916, 35, 493.

<sup>6</sup> *J. Soc. Chem. Ind.*, 1915, 34, 989.

<sup>3</sup> *Rubber Industry*, 1914, p. 212.

<sup>5</sup> Various papers, *Archief*, 1917 et seq.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> With a test ring 5 mm. thick and 4 mm. wide (cross-section over which stress is applied:  $2 \times 5 \times 4$  sq. mm.), the curve as ordinarily traced by the Schopper machine is to the scale—2 cm. = 100 per cent. extension, 1 cm. = 0.1 kg./mm.<sup>2</sup> load (ratio  $P/L = 1/2$ ). A more suitable scale is,

*Conventional expression of slope.*—For the purpose of expressing slope in a convenient manner, Schidrowitz and Goldsbrough give it as  $(L_{0.6} - L_{1.04})/2.5$ , where  $L_{0.6}$  and  $L_{1.04}$  indicate respectively the length at loads of 0.60 and 1.04 kg./mm.<sup>2</sup>. These points of reference are chosen for determining the inclination of the curve, because, except in the case of marked under- or over-cures, the stress-strain curve normally includes both these two points in its flat stage, so that extrapolation is unnecessary. For the ordinary types of plantation rubber (latex crêpe and sheet) the numerical value for slope seldom varies more than two or three units positively or negatively from a value of, say, 36. The extreme limits which the present author encountered in a survey of plantation rubbers of all types, including matured rubber and other types not generally found on the market, were 32 and 44. De Vries has encountered occasionally samples of markedly poor quality showing slopes in the neighbourhood of 50. De Vries,<sup>1</sup> who states that slope "is undoubtedly an important property," believes that it is the best property by means of which to classify rubber samples belonging to the low grades, where greater variations in slope are found than among latex rubbers.

The following table, given by Schidrowitz and Goldsbrough,<sup>2</sup> shows the position of the stress-strain curve at the two reference lengths mentioned above for the "correct" cure (cf. later) in a mix of 100 parts rubber : 8 parts sulphur, for each of the slopes generally encountered.

TABLE CIV

Slope	33	34	35	36	37	38	39	40	41	42	43	44	45
$L_{0.60}$	926	915	905	894	883	872	861	850	840	829	818	807	797
$L_{1.04}$	1008	1000	992	984	975	967	959	950	942	934	925	917	909
$(L_{0.6} - L_{1.04})$	82	85	87	90	92	95	98	100	102	105	107	110	112

say, 4 cm. = 100 per cent. extension, 5 cm. = 0.1 kg./mm.<sup>2</sup> (ratio  $P/L = 5/4$ ).

The highest load of which the Schopper machine allows is 100 kg. By taking a weight off the load lever, the load limit can be reduced to 50 kg. and at the same time the load scale can be doubled, while the length scale remains unchanged. This reduced load limit would not, however, be sufficient in many cases to break rings of 5 × 4 mm. cross-section. It may be suggested that, in order to get a curve with the present model of the Schopper machine on the larger load scale, a thinner ring, say, 3 mm. thick, might be adopted (cf. footnote 2, p. 288).

<sup>1</sup> *Archief*, 1918, 2, 485.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1919, 38, 347 T.



*Significance of slope.*—Clearly slope must be of significance in regard to the tensile properties of rubber in some of their aspects, although hitherto its significance has not been fully elucidated. As has appeared from the discussion in Chap. X of the general character of the stress-strain curve, the "flat" portion of the curve displays the quality of the vulcanizate in regard, predominantly, to tenacity. The inclination of this portion of the curve, *i. e.* the slope, representing the rate at which increasing load is increasing the extension, gives a measure of the resistance which the rubber is offering to further deformation. The smaller the slope, the greater is the resistance which the rubber is offering, and, at all events in regard to the tenacity characteristic of the last stage of the stretching, the better are the tensile properties of the rubber.

A noteworthy feature of the rubber curve, which an inspection of the figures given in the table (p. 351) reveals, has been pointed out by Shidrowitz and Goldsbrough<sup>1</sup>: the feature, namely, that the smaller (or better) the slope, *i. e.* the less rapid the extension with increasing load towards the end of the stretching, the more rapid is the extension at the beginning of the stretching. In other words, the smaller the figure for slope, the greater is the contrast between the steep and the flat portions of the stress-strain curve. It has already been pointed out (Chap. X) that the uniqueness of the tensile properties of rubber is to be seen perhaps most readily in a contrast, on stretching it, between its ready initial extensibility and its later tenacity. Hence, it may be said that the uniqueness of a sample of rubber—its characteristic rubber-like property—is more clearly marked, the lower the figure for slope determined by tracing the stress-strain curve of the sample.

Shidrowitz and Goldsbrough<sup>2</sup> draw attention, further, to a significance which the figures recorded in the above table have in regard to the use, for the purpose of comparing vulcanizates, of a method, which has sometimes been followed, consisting in determining the load necessary to produce a given intermediate extension, and then assuming that the greater the load, the better the vulcanizate. With rubbers of different slopes this last assumption may be the reverse of the truth. The load required to produce a given extension, or, alternatively, the extension produced by a given load, the determination of which fixes one point through which the stress-strain curve passes,

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

has strict validity as a method comparing the states of cure of different samples only when the samples have the same slope.

De Vries and Hellendoorn<sup>1</sup> have examined the relation of the properties which may be regarded as summed up by the value for slope to the recovery from stretching as shown by a sub-permanent set test. They found that the value for the slope of a number of samples of rubber gave, for the types of rubber ordinarily prepared,<sup>2</sup> a measure of their ability to recover from stretching.

*Mathematical expression for the stress-strain. Relation to the optimum cure.*—Slope enters as an essential feature into the treatment of the relation of the stress-strain curve to progressive curing which Schidrowitz and his co-workers have employed, with the intention of providing a theoretical basis for the conception of the Optimum Cure, and of defining the Optimum Cure more precisely in the case of individual samples of rubber.

Hatschek and Goldsbrough<sup>3</sup> find that the rubber stress-strain curve corresponds to a curve derived from a conchoid<sup>4</sup> by plotting the ordinates against a constant fraction,  $n$ , of the corresponding abscissæ. The ordinates ( $x$ , stress;  $y$ , strain) of the rubber curve are:—

$$y = a - b \sin \alpha,$$

$$x = n (a \cot \alpha - b \cos \alpha).$$

<sup>1</sup> *Vide* Chap. XIX, p. 450.

<sup>2</sup> A note may be added here. The samples in which de Vries and Hellendoorn observed a lack of exact correspondence between slope and set were, particularly, samples containing an amount of serum solids greater than usual. In these cases it appeared that the recovery was not so good as the low figure for slope would have suggested. The present writer is inclined to surmise that the inclusion of an unusual amount of serum solids in the coagulum, or possibly some other factor associated with the methods by which rubber containing more than the usual amount of serum solids has been prepared, produces an abnormal rise of several units in the slope which does not actually correspond to an equivalent improvement in the tensile properties; or, expressed otherwise, it may be necessary to apply a different scale in judging the significance of given numerical values for slope in connections with rubbers such as "slab" from that applied in connection with ordinary crêpe and sheet. The slope of ordinary crêpes and sheet seldom falls below 35. It would appear that for slopes from 35 up to 44 or more the slope is a fair index to certain tensile properties, but that for slopes below 35, such as are often found with slabs and other types of rubber containing a high proportion of serum solids, the slope cannot be taken as an index on the same basis.

<sup>3</sup> *Vide* Schidrowitz and Goldsbrough, *J. Soc. Chem. Ind.*, 1919, 38, 347 T.

<sup>4</sup> The conchoid curve passes through the mid-points of the radii-vectors drawn from a pole to an asymptote. Its ordinates are  $y = a - (b \sin \alpha)$ ;  $x = a \cot \alpha - b \cos \alpha$ , where  $a$  and  $b$  represent respectively the distance of the pole and the distance of the origin from the asymptote, and  $\alpha$  represents the angle which a radius-vector makes with the horizontal.

From a consideration of the significance of the terms in these expressions, Schidrowitz and Goldsbrough<sup>1</sup> conclude that that curve of any set of curves representing a series of progressive cures for which  $a = b$  represents a theoretically ideal balance of properties, and is to be considered as corresponding to the optimum, or, as they term it, the correct cure. The considerations in question are as follows: (1)  $a$  is the distance between the pole of the curve and the asymptote; (2)  $a.n$  is a constant for any given set of curves; (3)  $n$  represents the increase of stretch per increment of load, *i. e.* slope; (4) hence,  $a/a.n$  or  $1/n$  is the degree of stretch or extensibility; (5) it follows that  $a$  represents a quality which is the inverse of stretch capacity, *i. e.* toughness or tenacity; (6)  $b$  is the distance of the origin of the curve from the asymptote and represents the limit of extension.

Further, it was found, by solving the correct cure curves by the method of trial and error, that all correct cure curves are derived from a parent conchoid for which  $b$  (and, therefore, also  $a$ ) = 1050 per cent. Since the rubber curve meets the asymptote at infinity, it was concluded that all samples of *Hevea* rubber cured in a rubber-sulphur mix<sup>2</sup> will give at the correct cure curves which will meet at a point for which the co-ordinates are  $y = 1050$ ,  $x = \infty$ ; that is to say, that a length of 1150 per cent. is the limit of extensibility.

In order to decide which of a series of stress-strain curves represents the "correct" cure, it is necessary to determine  $a$ ,  $b$  and  $n$ , *i. e.* to determine (1) slope, (2) which is the particular curve for which  $a = b$ . For practical convenience the slope is taken as the increase in length, expressed in convenient units (see p. 351), between two fixed loads.

Now, it is clear that, since  $a.n$ , representing slope, may differ with different rubbers, the optimum curve ( $a = b$ ) will occupy a different position with rubbers of different slopes, being, Schidrowitz and Goldsbrough state, higher on the paper, the smaller the slope of the curve. According to this treatment, the position of the optimum curve is a function of the slope. The position of the curve for which  $a = b$  can be worked out once and for all for each of the slopes (limited in number; cf. Table CIV) encountered in practice.

*Slope and maximal tensile strength.*—While Schidrowitz and

<sup>1</sup> *Loc. cit.*

<sup>2</sup> The composition of the mix employed by Schidrowitz and Goldsbrough is rubber 100 : sulphur 8.

Goldsbrough's treatment of the stress-strain curves has not yet been fully investigated by other workers, the conclusions to which it leads find support in a recent research by de Vries and Hellendoorn into the maximal tensile strength developed by different samples of rubber in various rubber-sulphur mixes, to the extent that these latter authors have found that the optimum cure considered as the cure giving the maximal tensile strength is not represented in the case of all samples by a curve in the same position, but in the case of samples with markedly high (poor) slopes by curves in a lower position than in the case of samples with lower (better) slopes, such as average samples of latex crêpe or sheet.

Examples in this connection may be seen in Fig. 28 (p. 328). Samples 13, 90 and 240 represent latex crêpes with slopes, respectively, of 35, 36 and 37. Samples 355 and 356, the optimum cures of which, considered as the cures showing the maximal tensile strength, occur at very noticeably lower points on the paper, represent samples of wash-water crêpes with slopes, respectively, of 41 and 55. Three further samples (not shown in the figure), which were examined by de Vries and Hellendoorn in a mix containing 5 per cent. only of sulphur, showed the following as the position of the curve corresponding to the maximal tensile strength and the slope :—

TABLE CV

Slope	:	:	:	31	33.5	34
$L_{1.20}$	:	:	:	1167?	1126	1089

It appeared in de Vries and Hellendoorn's investigation that the cure giving the maximal tensile strength was for samples of ordinary latex crêpe and smoked sheet, having slopes ranging, say, from 35 to 38, represented by a curve having a position identical with or very close to the position which de Vries had adopted as a standard, viz. the position represented by a length of 990 per cent. at a load of 1.30 kg./mm.<sup>2</sup> It would appear, however, that for samples of the lower grades of rubber having steeper slopes the maximal tensile strength was shown by a cure the curve for which was lower down on the paper.

The degree of sharpness with which a maximum of tensile strength shows itself was not such, under the curing conditions to which the conclusions mentioned in the preceding paragraph refer—a rubber-sulphur mix, containing 7.5 per cent. of sulphur, and cured at 148°—to allow of the relation between the position

of the maximal tensile strength and the slope being examined more closely.

*The "correct" cure and a standard curve.*—It would appear, from Schidrowitz and Goldsbrough's treatment of the question—a treatment which, as has just been pointed out, derives a measure of experimental support from the work of de Vries and Hellen-doorn on the maximal tensile strength of rubbers of different slope—that the optimum curve cannot be taken in the same position for all samples of rubber. Yet the differences in the position of the optimum curve for rubber samples of different slopes are of an order, which is certainly not negligible, and which will demand consideration in future work aiming at exactness, but which, in the case of the ordinary range of plantation rubber samples, does not appear to be a very serious one. This conclusion is suggested by results of vulcanization tests based on the use of a single standard curve for all samples, which have been recorded by Eaton and by de Vries.<sup>1</sup> Results tabulated by the former<sup>2</sup> comprise data for several hundred samples, for each of which the optimum cure is given both as judged from the maximal tensile product and as judged from a standard curve. The number of cases was negligible in which the difference between the optimum cure as judged in one of these ways and that judged in the other was more than a quarter of an hour. Thus, an examination of the results given by 223 samples of latex crêpe sent in by estates shows that in one case the difference between the optimum time of cure based on the curve and that based on the breaking figures is half-an-hour, that in 86 cases there is no difference, and that in the remaining 136 cases the difference is given as one-eighth to a quarter of an hour. It should be noted that the curing intervals used in these tests were a quarter of an hour, and that the breaking figures were derived from the examination of two rings only at each cure.

#### CHENEVEAU AND HEIM'S EXPRESSION

The rubber stress-strain curve has also been treated mathematically by Cheneveau and Heim.<sup>3</sup> These authors find the

<sup>1</sup> The same conclusion is also suggested by results given by Schidrowitz and Goldsbrough (*loc. cit.* p. 352) comparing the "correct" cure with the maximal tensile strength and with the maximal tensile product. (Apparently the results in question are based on one test piece at each cure.)

<sup>2</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 398.

<sup>3</sup> *C.R.*, 1911, 152, 320; *Rubber Industry*, 1911, p. 327. Cf. Davies, *J. Soc. Chem. Ind.*, 1914, 33, 992; *J. Ind. Eng. Chem.*, 1914, 6, 985.

formula for the rubber stress-strain curves given by rubbers of all kinds—examples for which they quoted figures include “good rubber, no addition,” “middle-class rubber, moderately compounded,” “bad rubber, heavily compounded,” Para rubber, Vine rubber, Landolphia rubber—takes the form—

$$y = cx + a\sin^2 bx,$$

where  $y$  and  $x$  are the elongation and the load respectively, and  $c$ ,  $a$  and  $b$  are constants. In the view of Cheneveau and Heim the constants are characteristic of the elongation of the initial, the middle and the final portions, respectively, of the stretching, and are to be regarded as supplying precise numerical measures of the qualities, in rubber, indicated less precisely by the terms “suppleness,” “nervousness” and “tenacity” respectively.

The treatment of these authors, which need not here be analyzed with closeness, is from some aspects suggestive, but is not convincing at all points. The authors publish some preliminary data concerning attempts to compare the vulcanizing properties of samples of raw rubber by use of the above formula. Writing in 1911, they recognize the difficulty—at that date unsurmounted—which the existence of differences between samples in rate of cure presents when it is desired to make a comparison between different samples by means of vulcanization tests.<sup>1</sup> Although they adopt a fixed time and temperature of cure, they attempt to overcome the difficulty by curing with three different proportions of sulphur, viz. 2.5, 5 and 10 per cent.

At the best, the above equation does not offer a useful means of defining the optimum cure, and, hence, does not commend itself for the evaluation of raw rubbers in a given mix. It may be suggested, however, that it might prove of considerable value for comparing the stress-strain curves given by mixes of different composition, and obtaining numerical values for the tensile qualities expressed by such curves, so as to study, say, the effect of certain fillers on the qualities of rubber.

The application of the equation of Cheneveau and Heim does not appear to have been studied since the appearance of the original paper, except for a brief communication by Davies.<sup>2</sup>

<sup>1</sup> They confess: “It is a complicated matter to make comparison between a certain gum and Para, each being vulcanized under different best conditions.”

<sup>2</sup> But few attempts have been made to give suitable mathematical expression to the rubber stress-strain curve. In addition to the two attempts which have been discussed in the text, the only other attempts

## THE COEFFICIENT OF VULCANIZATION AND THE STATE OF CURE

Considerable discussion has recently ranged round the question of the use of the vulcanization coefficient as an index to the state of cure, and, especially, to the stability of the state of cure. The questions involved are not yet in a sufficiently advanced stage of exact investigation to allow of more than a preliminary and incomplete discussion in the present place.

Some writers have sought to lay down limits within which the vulcanization coefficient should fall at a correct cure. Spence<sup>1</sup> states that "the combined sulphur at the 'optimum cure' in the case of *Hevea* plantation rubber is a remarkably constant quantity, equal on the average to approximately 2.8-3 per cent. Where more than this amount of combined sulphur has been found, either the method of vulcanization is at fault or the means of determining the 'optimum cure' is inaccurate.<sup>2</sup> . . . So constant indeed is the value of the combined sulphur at the correct cure in the case of *Hevea brasiliensis* rubber, that we have come to regard the relation between rubber and sulphur as stoichiometric, representing a more or less definite compound of rubber and sulphur to which a formula may be assigned, on the assumption that the partial valences of the rubber-aggregate have not all the same affinity for sulphur." Spence has not, however, published any experimental results relative to the question; nor does he define the sense in which he uses the term "optimum cure." Stevens<sup>3</sup> has stated, in connection with his investigation of the stability of vulcanizates, that "a figure for the coefficient of vulcanization exceeding 3.5 [elsewhere he mentions 3.2] in the case of a rubber and sulphur compound is an almost certain indication of over-curing."

It does not appear, however, that there is any evidence available which would enable a "correct" vulcanization coefficient

appear to be those of Schmulewitsch and of Ono. The former of these two authors (*Vierteljahresschr. d. naturf. Ges. in Zürich*, 11, Heft 3; *Ann. der Phys.*, 1871, 144, 280) gives the elongation,  $y$ , corresponding to a load,  $x$ , as  $y^2 = ax^2 + bx$ . But he examined only the very early stages of the stretching. Ono (*Proc. Mathematico-Physical Soc., Tokyo*, 1913, 7, 36; *Sc. Abstrs.*, 1913, A, 451) gives  $S = A[1 - 2/(\lambda - \beta)] e^{h/2 \cdot \lambda^2}$ , where  $S$  is the stress per unit of original area,  $\lambda$  the strained length/original length,  $\beta$  strained breadth/original breadth, and  $A$ ,  $h$  and  $p$  are constants.

<sup>1</sup> *I.R.J.*, 1916, p. 861 (Dec. 9).

<sup>2</sup> Spence makes the proviso that the curing should be carried out "in a minimum of time with the least possible injury to the molecule."

<sup>3</sup> *J. Soc. Chem. Ind.*, 1916, 35, 874; *I.R.J.*, Feb. 10, 1917; *J. Soc. Chem. Ind.*, 1918, 37.

of universal applicability to rubber compounds to be laid down. Rather, the available data indicate that the vulcanization coefficient at what may be regarded, at least in the present condition of our exact knowledge, as comparable states of cure varies considerably with the curing conditions, the character of the raw rubber sample (attention is confined to *Hevea* rubber) and the character of the materials which may be mixed with the rubber.

(a) *Influence of organic accelerators on the vulcanization coefficient.* In experiments by the Delft Institute<sup>1</sup> with the accelerator *p*-nitrosodimethylaniline, it was clearly indicated that the vulcanization coefficient corresponding to a given state of cure, as judged by the position of the stress-strain curve, was smaller for a rubber-sulphur mix containing the accelerator mentioned than for the same mix from which the accelerator had been omitted.

The present writer (unpublished experiments with O. J. Walker) found the vulcanization coefficient at the cure of a 90/10 rubber-sulphur mix giving the maximal tensile strength to be noticeably lower in the presence of 1 per cent. of piperidine-piperidylthiocarbamate than in its absence. The experiments covered a number of different temperatures. At 141° the corresponding coefficients were 3.54, 4.31. Cranor<sup>2</sup> also finds that the addition of an organic accelerator reduces the figure for combined sulphur at cures giving good mechanical properties. Kratz and Flower<sup>3</sup> similarly give it as their experience that accelerators reduce the vulcanization coefficient at the cure giving the maximal breaking figures.<sup>4</sup>

(b) *Influence of the character of the rubber.*—Eaton<sup>5</sup> concludes, with reference to progressive cures at 141° in the mix rubber 90 : sulphur 10 " that slow-curing (crêpe) rubbers contain between 3.7 and 4.1 per cent. combined sulphur at optimum time of cure and fast-curing (slab) rubbers 4.2–4.6 per cent., sheet or

<sup>1</sup> *Meded. Delft*, 1916, p. 117; *Delft Communics.*, p. 213.

<sup>2</sup> *J. R. W.*, 1919, 61, 137.

<sup>3</sup> *Chem. Met. Eng.*, 1919, 20, April 15.

<sup>4</sup> These authors show (*loc. cit.*) a mix consisting of rubber, sulphur and an unidentified accelerator in the ratio 90 : 10 : 1.25 as having a vulcanization coefficient of 3.00 at a cure of sixty minutes at 281° F. (138.3° C.). This cure appears to be below the optimum. (It is about ten minutes on de Vries' scale away from the optimum cure.) The vulcanization coefficient indicated for the optimum cure is *ca.* 3.2—a figure considerably lower than the figures obtained by Eaton for the optimum cure in mixes similar to the above except for the absence of an added accelerator.

<sup>5</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, pp. 134 *et seq.*



medium-curing samples being intermediate." Eaton's tabulated data refer to forty samples only, ranging in curing time from 1-3.5 hours. They hardly seem sufficient to warrant the above statement being accepted as generally true. If, however, it is true that rapid-curing samples of raw rubber give a higher vulcanization coefficient at the optimum cure than slow-curing ones, it would seem that the effect, in regard to the rate of combination of sulphur when curing to optimum tensile properties, of the natural accelerators is opposed to that of artificial organic accelerators.<sup>1</sup>

(c) *Influence of percentage of sulphur and of the temperature of vulcanization.*—It will be seen from what has gone before that it is not possible to lay down on the basis of the available evidence a general principle to the effect that the more rapid the vulcanization, the smaller the vulcanization coefficient at the optimum cure; although the general apprehension is in the sense of such a principle. If such a principle were found to be acceptable, it would be expected that the vulcanization coefficient at the optimum cure would be influenced (negatively) by increase in the percentage of sulphur in the mix or by increase in the vulcanization temperature. There is no sufficient evidence to enable it to be said whether the percentage of sulphur and the vulcanization temperature do in fact influence the vulcanization coefficient in this way. It may be noted that Eaton's figures, referred to in the preceding paragraph, for the vulcanization coefficient at the optimum cure in rubber-sulphur mixes, containing 10 per cent. of sulphur and cured at 141°, are noticeably lower than de Vries' figures for the vulcanization coefficient at the optimum cure in rubber-sulphur mixes containing less (7.5 per cent.) sulphur, but cured at a higher temperature (148°).

(d) *Influence of the presence of inorganic additions.*—It appears that in technical mixes the magnitude of the vulcanization coefficient at the optimum cure, defined as the cure giving the maximal tensile product, varies considerably according to the composition of the mix, and is generally much lower than the corresponding figure for rubber-sulphur mixes containing similar proportions of sulphur (referred to the rubber present). Comparatively few systematic data have been published on this

<sup>1</sup> Perhaps not all organic accelerators. It is possible that different organic accelerators may act differently in regard to the rate of combination of sulphur. Preliminary experiments of the author (which require confirmation) indicate that the vulcanization coefficient at the optimum cure may be raised by hexamethylenetetramine.

subject, although a good deal of experience relative to it has, naturally, been accumulated in rubber works. Data have been published which show that the addition to rubber and sulphur of inorganic materials used so commonly in technical practice as zinc oxide, magnesium oxide, litharge and lime lead to a much lower value for the vulcanization coefficient at the optimum cure than would be found in their absence.<sup>1</sup>

Kratz and Flower<sup>2</sup> found the vulcanization coefficient<sup>3</sup> for a mix containing first latex plantation crêpe, zinc oxide, sulphur, and an amine in the ratio 100 : 100 : 5 : 0.33 to be 1.69 for an optimum cure of sixty minutes at 298° F. (148°). (See Table CXVIII.) In another experiment the same authors<sup>4</sup> give as the vulcanization coefficient of a mix similar to the above with the omission of the amine 3.075 for an optimum cure of 120 minutes at 298° F. (see Table CVI). They also find that the introduction of magnesia into such a mix markedly reduces the vulcanization coefficient at the optimum cure; and that the introduction of lime appears to reduce it when the lime is present in small amount, and raise it again when present in large amount. Their results are shown in Table CVI. The control mix consisted of 100 parts rubber, 100 parts zinc oxide, and 5 parts sulphur. The other mixes were made by substituting for some of the zinc oxide the quantity of inorganic accelerator shown.

The data, shown in Table CXIX, p. 389, obtained by Fol and van Heurn in the vulcanization of mixes containing zinc oxide, magnesia and litharge, may also be examined in this connection. They indicate that the vulcanization coefficient at the cure giving a tensile product which is maximal or nearly so may be very

<sup>1</sup> It is possible to conceive that in a mineralized mix, viewed from one aspect, the function of the "mineral" is to supply the tenacity and the function of the rubber to supply the extensibility; so that a correct cure of the whole, corresponding to an optimum balance of tensile properties, may correspond to an under-cure of the actual rubber present, and thus to the combination of a smaller proportion of sulphur than at the optimum cure in the absence of the mineral. Whether such a conception would be just cannot at present be said.

<sup>2</sup> *J. Ind. Eng. Chem.*, 1919, **11**, 30.

<sup>3</sup> The quantities given by Kratz and Flower are not actually vulcanization coefficients, considered as the amounts of sulphur in combination with the rubber expressed as percentages of the rubber, but are quantities of sulphur in combination with the rubber and the inorganic constituents expressed as a percentage on the rubber. They are designated by these authors "sulphur coefficients." (Cf. the section "Fixation of Sulphur by the Mineral Constituents," p. 389).

<sup>4</sup> *Chem. Met. Eng.*, 1919, **20**, April 15.

much below the vulcanization coefficient at a corresponding cure in a mix of rubber and sulphur only.

TABLE CVI

Accelerator.	Parts accelerator.	Time of optimum cure (min.).	P <sub>B</sub> .	L <sub>B</sub> .	Vuln. coeff.
None . . . . .	0	120	1.331	725	3.075
Heavy calcined magnesia {	5	90	1.553	700	2.586
	10	75	1.627	725	1.723
Light magnesia . {	5	90	1.322	700	2.780
	10	45	1.875	750	2.184
Lime . . . . . {	5	90	1.294	800	1.990
	10	45	1.565	750	2.926

*The vulcanization coefficient as an index to the state of cure.*—The state of cure of different samples of rubber in a given rubber-sulphur mix, as expressed by the stress-strain curve, is indexed with moderate but not complete exactness by the vulcanization coefficient. Van Rossem<sup>1</sup> has correlated the results, for the vulcanization coefficient and the position of the stress-strain curve (registered by the load required to produce an extension of 850 per cent.), obtained at the Delft Institute when curing a large number of plantation samples for 1.5 hours at 148° in the mix rubber 92.5 : sulphur 7.5. The correlation table for a collection of 346 samples, including 237 latex crêpes and 109 smoked sheets, is shown on the opposite page.

A high degree of correlation between the vulcanization coefficient and the position of the stress-strain curve was further shown by the value ( $+0.851 \pm 0.016$ ), calculated by van Rossem for the correlation coefficient for the vulcanization coefficient and the stress required to produce an elongation of 400 per cent. on the Schwartz machine (see p. 417) from the data for 128 samples vulcanized under the conditions already mentioned. De Vries<sup>2</sup> remarks that, on plotting the breaking points and the vulcanization coefficients of 137 samples, extensive data for which, obtained by the Delft Institute at its standard cure, are given by Fol,<sup>3</sup> he finds that the difference in the vulcan-

<sup>1</sup> *Loc. cit.*, p. 108.

<sup>2</sup> *I.R.J.*, 1917, p. 108.

<sup>3</sup> *Rep. Batavia*, p. 190.

ization coefficient for any given position of the curve seldom exceeds 0.5. Only in five or six cases is the difference greater, and in no case is it more than 0.9.

TABLE CVII  
*Vulcanization coefficient*

Load (kg./mm. <sup>2</sup> ) for elongation of 850 per cent.	1'45- 1'95	1'95- 2'45	2'45- 2'95	2'95- 3'45	3'45- 3'95	3'95- 4'45	4'45- 4'95	4'95- 5'45	5'45- 5'95
0.255-0.405	7	25	4	1					
0.405-0.555	4	18	37	17	6				
0.555-0.705		2	19	35.5	19	7			
0.705-0.855			3.5	14	27.5	11			
0.855-1.005			1	3	12.5	21	7		
1.005-1.155					2	10.5	10.5	1	
1.155-1.305						1	3	5	1
1.305-1.455								4	2
1.455-1.605								1	2

Correlation coefficient =  $+0.867 \pm 0.009$ .

Eaton and Day<sup>1</sup> find the vulcanization coefficient at the optimum cure of a number of crêpe, sheet and slab samples to range from 3.7-4.6 per cent. De Vries<sup>2</sup> also found the vulcanization coefficient at the optimum cure to have a range of about 1 per cent. De Vries and Hellendoorn<sup>3</sup> state, regarding the change of the vulcanization coefficient with progressive curing, that "the figures run exactly parallel to the 'length at 1.30 kilos.'"

Stevens,<sup>4</sup> who also has investigated the relation of the vulcanization coefficient to the position of the stress-strain curve, finds results in agreement with the statement of de Vries and Hellendoorn for crêpe and smoked sheet; but concludes that in the case of matured coagulum (slab) the relation between the vulcanization coefficient and the position of the stress-strain

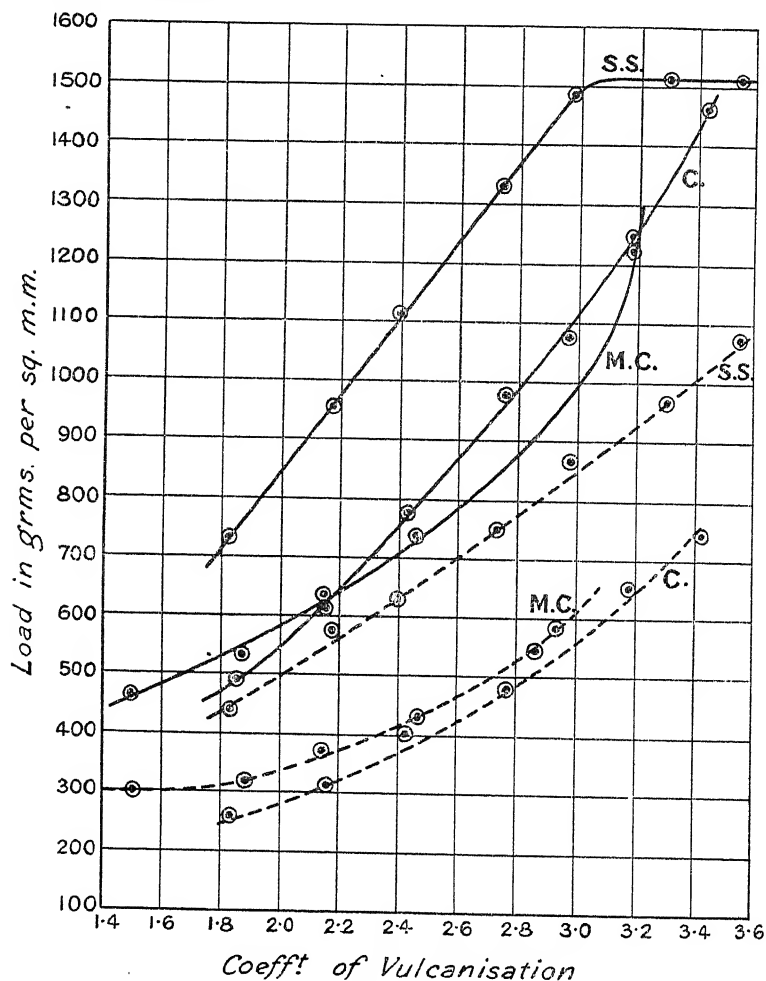
<sup>1</sup> *J. Soc. Chem. Ind.*, 1917, 36, 1118.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1917, 36, 1258.

<sup>2</sup> *Loc. cit.*

<sup>4</sup> *Ibid.*, 1918, 37, 280.

curve is not a linear one. Stevens' results are summarized in the following figure:—

FIG. 33.<sup>1</sup>

S.S. = smoked sheet; C = crêpe; M.C. = Matured coagulum  
 - - - -  $P_{900}$ ; —  $P_{1000}$ .

<sup>1</sup> From the *Journal of the Society of Chemical Industry*. This figure, it may be remarked *en passant*, would appear to show the influence of the lower slope, which de Vries has found (see p. 193) to characterize matured rubber as compared with unmatured. For, whereas the curve for matured rubber here lies above the curve for crêpe for measurements at  $L = 900$ , it lies for the most part below the latter for measurements at a greater length, viz.  $L = 1000$ .

The bend seen towards the end of the curve for the smoked sheet, which otherwise is a straight line, requires confirmation. The samples of raw rubber used in this investigation were composite samples; the intention being to make each more or less of the type of rubber in question. The mix was rubber 90 : sulphur 10, and the vulcanizing temperature 35 lb. steam pressure. For registering the position of the stress-strain curve, the stresses required to produce lengths of 900 and of 1000 per cent. were measured. The stresses recorded in the figure are the mean of measurements, made at room temperature, after one day's rest and after seven days' rest at a temperature of 13° and at a temperature of 28°.

Concerning the question as to how far the vulcanization coefficient rather than the mechanical properties can or should be used as a measure of the state of cure for practical purposes, it may be said that, since the practical value of vulcanized rubber in almost all connections lies in its mechanical properties, the ultimate criterion of the state of cure for practical purposes must be sought in the mechanical properties. The vulcanization coefficient, while not the ultimate practical criterion of the state of cure, may, however, form in some circumstances a valuable index to it. For practical purposes it is not a convenient index in the case of simple rubber-sulphur mixes, containing comparatively large amounts of sulphur (say, 7.5-10 per cent.), which, as pointed out at the conclusion of the succeeding chapter, probably form the most suitable basis for the comparative evaluation of raw rubbers; because, in the case of such mixes, the stress-strain curve is a more delicate and—as may be judged from, for example, the comparatively wide range of variation in the vulcanization coefficient at the optimum cure in such mixes—unambiguous guide to the state of cure than is the vulcanization coefficient. Further, there is the important practical consideration that the analytical operation of determining the vulcanization coefficient is, although not complicated, lengthy. In mixes, such as those discussed in Chap. XVI, containing inorganic ingredients, the case is different from that in rubber-sulphur mixes containing high proportions of sulphur. As will be apparent from the data given in that chapter, while the tensile properties may change only slightly or may remain almost unchanged over a wide range of cures, the vulcanization coefficient may change continuously; and, hence, the vulcanization coefficient may present itself as a more delicate index to the

state of cure than do the tensile properties. In the present state of investigation, regarding the tensile properties of mineralized mixes, and particularly where, as is often the case in rubber factories, the investigation of the tensile properties is limited to determinations of breaking-points and does not include tracing the stress-strain curves, the vulcanization coefficient is a more sensitive index to them than are the figures for tensile properties.<sup>1</sup> It may be hoped, however, that, with the future development of the exact mechanical testing of mineralized vulcanizates, it will be possible to find in a tensile or other mechanical test a means of distinguishing between progressive cures as delicate as (and, of course, more rapid than) the vulcanization coefficient.

<sup>1</sup> Cranor (Meeting of the Rubber Section of the Amer. Chem. Soc., September 1918), apparently with mixes containing inorganic constituents chiefly in mind, has stated as his conclusion that "the determination of the coefficient of vulcanization is a valuable and accurate check on the cure of a stock, the composition and history of which is known." He adds, it may be noticed: "It should not be used arbitrarily as a standard of comparison of differently treated stocks, even if they are of the same general nature."

## CHAPTER XV

### STABILITY OF STATE OF CURE

ONE of the prime desiderata in the preparation of vulcanized rubber for technical purposes is that the product shall be as stable as possible: that it shall not, for example, become brittle or "perished" on keeping. Vulcanized rubber appears always to be a more or less unstable material. The lack of constancy in the behaviour of rubber may be considered as displaying itself in, broadly, two ways. (a) Prior mechanical operations influence the result of subsequent ones.<sup>1</sup> Actual numerical data concerning such influence may be found in the work, discussed elsewhere in this volume, of Kohlrausch on torsional after-effect, of Schwartz on hysteresis, and particularly of Bouasse on the succession of cycles of extension and retraction and on the magnitude of the modulus of elasticity under various conditions. (b) A secular change of the vulcanizate, apart from its mechanical history

In the case of rubber goods in actual use, the results of factors falling under these two heads doubtless modify each other to a very considerable extent. "Ageing" involving the influence both of subjection to a succession of mechanical deformations and the mere passage of time has not yet been the subject of any systematic study. The "ageing" tests hitherto employed have involved only the examination of the mere passage of time on rubber kept in an undeformed condition, either at ordinary temperature, or, in the case of "accelerated ageing tests," at a somewhat elevated temperature.

Ditmar,<sup>2</sup> in the course of some remarks on vulcanized rubber as a colloidal system, presents the inconstancy of the material in somewhat striking phrases. He refers to the freshly-vulcanized

<sup>1</sup> It should be mentioned that in experimental work on the evaluation of raw rubber, such as that discussed in the preceding three chapters, the vulcanizate is always taken for tensile tests without being subjected to any prior deformation.

<sup>2</sup> "Welchen praktischen Wert haben mechanische Prüfungen des Kautschuks?"—*Koll. Zeit.*, 1912, **10**, 238.



rubber as a "living" colloid<sup>1</sup> and that it becomes "dead," i.e., completely dead, when it is left lying aside for many years. However, it is not true that the dead system can be awakened by stretching and rubbing. The rubber which has been transformed again into a dispersive system, as when a bicycle is brought out into the open after lying in the garage, the tyre is hard and dead. The rubber, like the human sleeper, the heat, the expansion of the air, the increase in the pressure of the load, awaken the system. It is as if the life remains at its best, if it is kept warm, if it is kept under the experience of the motorist and the bicycle pump.

Colloids bear the greatest analogy to living organisms, indeed based on colloids, and it is therefore not surprising. We can speak of a life curve of rubber, and this has great history in the latex, in the mixing in the sheets, in the aging in the storage. This life curve becomes flatter and flatter (aging phenomena), until it ends in the death and decay of the colloidal system. That is the fate of all colloids, even the vegetable and the animal cell lose its capacity to grow and to develop, lignification, shrivelling in old age in man and beast.<sup>2</sup>

#### EXPERIMENTAL AGEING

The exact investigations into the ageing of vulcanized rubber hitherto made are not very numerous. Störing, who compares vulcanization to an *impulse* the effects of which are felt after the conclusion of the actual heating, has investigated the change at ordinary temperature of the breaking points of vulcanizates representing progressive cures at 114.5° of mixes consisting of crêpe, sheet and of matured coagulum, with sulphur in the ratio rubber 90: sulphur 10. He found the vulcanizates obtained from this mix, which is the type of mix widely used in experimental work, to display very marked instability in their breaking

<sup>1</sup> "Wir können von einer Lebenskurve des Kautschukbalkens sprechen, die ihre Vorgeschichte im Latex, im Mischen, in der Vulkanisation und im Lagern hat. Diese Lebenskurve wird flacher und flacher. Alterserscheinungen) bis sie zum Tode des kolloidalen Systems zur Vulkanisation führt. Das ist das Schicksal aller kolloidalen, auch die pflanzliche und tierische Zelle entquillt, sie altert, blüht, blättert, Vertheilung, Zusammenschlumpfen im Alter bei Tier und Mensch. *Loc. cit.* 241, 242. Das unvulkanisierte und vulkanisierte Kautschukbalken verhält sich im Bezug auf seinen physikalischen Zustand nicht viel im Laufe einer Zeitperiode, es verhält sich sozusagen ununterbrochen. *Ibid.*"

points. The instability was very marked indeed in the case of cures giving in the first instance, when tested shortly after being made, maximal breaking figures, and was still more marked in the case of longer cures. The following table shows typical results, obtained with a sample of latex crêpe.<sup>1</sup>

TABLE CVIII

Cure (hrs.)		2	2.5	3	3.5	4	4.5
	Age in days.						
	4	0.96 × 1151	1.23 × 1098	1.51 × 1078	1.69 × 1013	2.01 × 987	2.48 × 953
	125	0.95 × 1016	1.55 × 1017	1.61 × 991	1.93 × 952	1.76 × 897	1.76 × 851
$P_B \times L_B$	203	1.01 × 1046	1.50 × 1032	1.63 × 1004	1.74 × 936	1.48 × 858	0.49 × 611
	311	0.92 × 1035	1.40 × 1009	1.64 × 993	1.48 × 894	1.33 × 822	0.17 × 372
Vulc. coeff.		2.0	2.6	3.2	4.1	4.5	5.0

In some further experiments by Stevens,<sup>2</sup> the period during which observations were made extended to 120 weeks; and the vulcanization coefficient was determined at the beginning and at the end of the period of ageing. Samples of sheet, slab and crêpe were examined. It was concluded that the more advanced the state of cure as indicated by the vulcanization coefficient, (a) the greater was the increase in the vulcanization coefficient on ageing, and (b) the more rapidly did the breaking figures of the vulcanizate begin to fall. This is shown by the data in the following table, which summarizes the results of tests on six samples of rubber belonging to the types just mentioned.

TABLE CIX

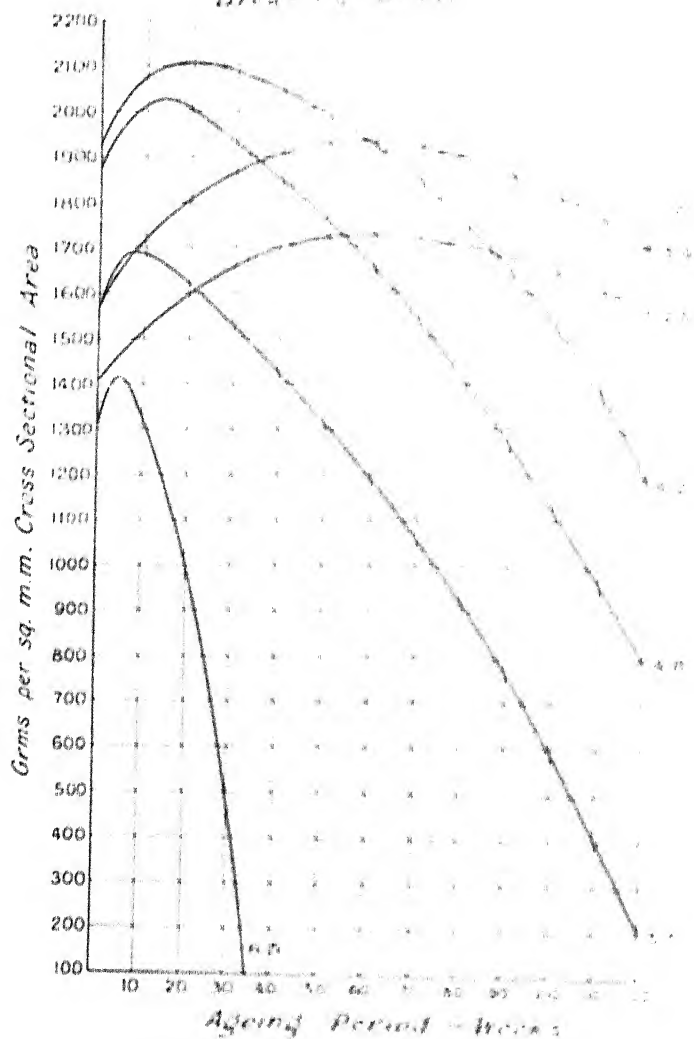
Mean coefficients between . .	2 & 3	3 & 4	4 & 5	5 & 6	over 6
Mean increase in coeff. during ageing period	0.02	0.10	0.25	0.51	—
Maximum $P_B$ shortly after vulcanization	1.56	1.93	2.09	1.79	1.58
Mean period (weeks) during which $P_B$ increased	54	33	10	3	nil

The following figure shows results for one sample which may be taken as typical.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, 35, 872.

<sup>2</sup> *Ibid.*, 1918, 37, 305, 340.

*Smoked Slab*  
*Break - 3 Sticks*

FIG. 14<sup>1</sup>

The cures to which this figure refers were for the same length of time as those shown in Table XVIII. It will be observed that, on keeping, all cures show an initial increase in breaking stress.

<sup>1</sup> From the *Journal of the Society of Chemical Industries*. The sample of smoked slab here in question appears to be considerably slower curing than the average sample of unsmoked slab.

and a subsequent fall; and that the more advanced the state of cure as indicated by the vulcanization coefficient, the more quickly is the highest point in regard to tensile strength reached by the vulcanizate, and the more rapid is the collapse. In the case of the less-advanced states of cure (vulcanization coefficient, 2.8 and 3.4), the fall from the maximum is slow, and, within the period of the observations, the tensile strength has not, as in more advanced states of cure, fallen to a point indicative of comparative brittleness, but, rather, is still at a higher point than its initial value. In the case of some samples of rubber, the tensile strength of cures showing vulcanization coefficients between 2 and 2.5, after rising to a maximum, remained practically constant to the end of the period of observation.

The cures, showing vulcanization coefficients of less than *ca.* 3, the tensile strength of which changed least during the period of observation, and which were, by contrast with cures showing higher coefficients, comparatively stable, were cures at which the tensile strength developed was below the maximum for the mix in question, *i. e.* were cures under the "optimum" cure, which, as hitherto defined, would be placed at a point showing a vulcanization coefficient between 4 and 5.

#### ACCELERATED AGEING

The proposal, made by Geer,<sup>1</sup> to employ, in certain connections, for the purpose of studying the stability of vulcanizates, an "accelerated ageing test," consisting in heating the vulcanizate in a current of warm air, at a temperature of, say, 70°, has received considerable acceptance.

*Spence's observations on the rate of combination of sulphur at low temperatures.*—The progress of vulcanization at temperatures, such as the temperature just mentioned, much below those employed technically for vulcanization was first investigated closely, in regard to the combination of sulphur, by Spence, in the course of his work on the theory of vulcanization.<sup>2</sup> The following is some account of Spence's results<sup>3</sup>:—

A. Two mixes, I and II, consisting of rubber and sulphur only, and containing about 9 per cent. of the latter, were

<sup>1</sup> *I.R.W.*, 1916, 55, 127.

<sup>2</sup> For an earlier and briefer investigation, *vide* Hinrichsen, *Koll. Zeit.*, 1911, 8, 245.

<sup>3</sup> Spence, *Koll. Zeit.*, 1912, 10, 299; Spence and Young, *ibid.*, 1913, 13, 265.

examined. The rubber in Mix I consisted of well-purified rubber; it vulcanized slowly and deteriorated quickly. Mix II was rapid-curing, and the vulcanizates showed no tendency to deteriorate.<sup>1</sup> In each case the unvulcanized mix, the under-vulcanized, normally-vulcanized and over-vulcanized<sup>2</sup> product was examined. Whether the material was kept in the dark or in sunlight, no sulphur noticeably greater in amount than the possible experimental error could be detected as entering into combination during three months at ordinary temperature in the case of any of the products from Mix II, except in the case of the over-vulcanized sample. In the case of the Mix I, under the same conditions, there was no appreciable combination of sulphur in the unvulcanized material, but a noticeable further combination of sulphur in all the vulcanized products. At 40° an appreciable amount of sulphur combined during the three months' interval in all cases; although in the case of the unvulcanized materials and all the vulcanized products from Mix II, except the over-cured one, the amount was very small. The results are shown in the following table.

TABLE CX<sup>3</sup>

*Increase in combined sulphur (per cent.) during 3 months*

		Un-vulcanized.	Under-vulcanized.	Normally-vulcanized.	Over-vulcanized.
Mix I	In the dark . . .	0.05	0.66	0.69	0.65
	In sunlight . . .	0.07	0.59	0.62	0.59
	In thermostat at 40° . .	0.11	1.09	1.14	1.11
Mix II	In the dark . . .	0.01	0.093	0.113	0.388
	In sunlight . . .	0.051	0.025	0.037	0.267
	In thermostat at 40° . .	0.157	0.21	0.299	0.535

None of the samples from Mix II had, to judge by their appearance, suffered change during the period of three months. In all the vulcanized samples from Mix I considerable deterioration was apparent. This deterioration could be observed in the

<sup>1</sup> Further details concerning the rubbers used are not given.

<sup>2</sup> The degree of vulcanization of the product was judged apparently by factory experience.

<sup>3</sup> The combined sulphur was determined, after forty-eight hours' acetone extraction, by the Carius method.

The samples exposed to sunlight all showed a reduction of their total sulphur content.

The initial total sulphur contents of the materials were as follows: Mix I: 8.88, 8.53, 8.60, 8.46; Mix II: 8.93, 9.01, 9.06, 8.99 per cent.

physical properties of the samples, and the following table shows that it was also reflected in the resin-content (difference between the acetone extract and the combined sulphur).<sup>1</sup>

TABLE CXI

Per cent.	Mix I.				Mix II.		
	Un-	Under-	Normally-	Over-	Un-	Under-	Normally-
		vulcanized.	vulcanized.	vulcanized.		vulcanized.	vulcanized.
Initial resin-content	1.06	1.31	1.82	2.18	2.53	2.78	2.85
Change during 3 months in dark	+0.31	+3.24	+2.72	+1.48	-0.17	-0.54	-0.55
Change during 3 months in sunlight	+0.40	+3.23	+2.92	+1.60	+1.32	+0.80	+0.65
Change during 3 months at 40°	+0.42	+3.56	+2.96	+1.79	-0.24	-0.42	-0.59

B. Samples of two mixes, III and IV, of the same general character as the above Mix II, and containing about 9 per cent. of sulphur, were sealed in glass tubes and heated in thermostats at the temperatures and for the periods of time shown in the following table.

TABLE CXII

		Temperature of vulcanization.				
		50°	65°	80°	95°	110°
<i>Mix III</i>	1 day (24 hrs.)	0.19	0.26	0.48	4.74	9.24
	3 days	0.39?	0.50	1.26	7.76	9.37
	6 "	0.25	0.72	2.45	9.42	9.52
	9 "	0.27	0.87	3.85	9.53	9.49
<i>Mix IV</i>	1 day	0.14	0.28	0.33	1.26	7.25
	3 days	0.21	0.38	0.95	4.47	9.36
	6 "	0.18	0.28	1.71	8.49	9.37
	9 "	0.19	0.31	2.27	9.16	9.37

C. Two mixes consisting of 90 parts of plantation rubber and 10 parts of sulphur were prepared. The rubber employed in the first mix had been extracted with acetone. And it proved that the rate of combination of sulphur at low temperatures was excessively slow in the case of such rubber—after 90 days'

<sup>1</sup> Subsequent investigations into ageing have not included "resin" determinations. Further data on the possible change of resin-content with ageing would, however, be of interest.

heating at 75° only 0.32 per cent. of sulphur has entered into combination. The second mix was similar to the first, except that 1 per cent. of the acetone extract was introduced into it. Samples, contained in sealed tubes, were heated in thermostats. They gave the following results :—

TABLE CXIIA  
*Percentages of combined sulphur*

		Temperature of vulcanization.					
		50°	55°	60°	65°	70°	75°
Period of vulcanization.	5 days (24 hrs.)	0.04	0.08	0.098	0.197	0.384	0.495
	15 "	—	—	—	0.564	1.13	1.71
	25 "	0.15	0.36	0.57	—	—	—
	35 "	—	—	—	1.46	2.60	3.80
	50 "	0.25	0.65	1.03	—	—	—
	65 "	—	—	—	2.55	4.91	7.42
	80 "	0.45	1.10	1.86	3.37	6.05	8.81
	90 "	—	—	—	—	—	9.36

The temperature coefficient of the reaction between rubber and sulphur at low temperatures as calculated from the above figures is substantially the same (mean = 2.84) as that calculated from figures obtained by Spence and Young<sup>1</sup> for vulcanization at 135° and at 155° (mean = 2.65).

The figures for combined sulphur at each temperature given in the above table, when plotted against time, fall with considerable exactitude on straight lines, with the exception of the last two figures at 75°, which make the curve corresponding to 75° bend at its end towards the time axis (cf. p. 313).

The results of Spence would indicate that at ordinary room temperatures no appreciable increase in the vulcanization coefficient of a vulcanizate will occur within any ordinary period of observation. Such was found to be the case in observations made by the Delft Institute.<sup>2</sup> Samples of rubber which had been vulcanized for 1.5 hours at 148° in a rubber-sulphur mix containing 7.5 per cent. of sulphur were stored for one year in a cool, dark place; and their vulcanization coefficients were determined before and after storage, with the following results. (Cf. Stevens' results, p. 369.)

<sup>1</sup> *Koll. Zeit.*, 1912, 11, 32.

<sup>2</sup> *Meded. Delft*, 1916, p. 123; *Delft Communics.*, p. 219.

TABLE CXIII

Sample No.	1	2	3	4	5	6
Original coefficient	5.00	5.40	4.61	4.11	2.87	2.78
Coefficient after 1 year	5.05	5.64	4.71	4.38	2.76	2.78

*De Vries' observations on change of stress-strain relations at temperatures above the atmospheric.*—De Vries, working with mixes of plantation rubber and sulphur, containing 7.5 per cent. of the latter, and cured at 148°, has studied "accelerated ageing." His studies deal particularly with the change in tensile properties, but also include determinations of the change in combined sulphur and some comparisons of "accelerated ageing" and ageing at ordinary temperatures.<sup>1</sup> It was concluded that, on keeping a vulcanizate at ordinary (tropical) temperature, while there was no appreciable increase in the combined sulphur, the stress-strain curve moved down the paper, as in continued vulcanization. Two examples quoted by de Vries are as follows :—

TABLE CXIV

Time elapsed since vulcanization	Sample 22H.		Sample 422.	
	3 days	163 days	3 days	171 days
Combined sulphur (per cent.)	5.45	5.43	5.75	5.86
$L_{1.30}$	964	901	982	928

Eaton and Grantham<sup>2</sup> had observed a change of a similar order in the position of the stress-strain curve, on keeping vulcanizates at ordinary temperatures. They concluded, from observations on mixes of rubber 90 : sulphur 10 cured at 141°, that during the period from three days after vulcanization to almost six months later the curve changed its position in the case of under-cured, correctly-cured and slightly over-cured samples by an amount representing an extra cure of about a quarter-of-an-hour.

De Vries states that "it is not necessary to make experiments for so many months at the ordinary temperature. The same effect is reached in a few days at temperatures of 70 or 75°; the curve proceeds down the paper, just as it does when the time of cure is lengthened, but the percentage of combined sulphur remains the same." De Vries has studied the slow vulcanization which "accelerated ageing" may be regarded as representing;

<sup>1</sup> *I.R.J.*, 1917, **53**, 101; *Archief*, 1918, **2**, 792.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 715.



and has compared its effect on vulcanizates cured to a point below the maximum of tensile strength with the effect of continued vulcanization at an ordinary vulcanizing temperature (148°). He finds that the curve changes its position in "accelerated ageing" in exactly the same way as in continued curing, but that the maximal tensile strength developed is smaller. He finds, further, that the change in tensile properties occurring on accelerated ageing is unaccompanied by any increase in the amount of combined sulphur, such as that which occurs with continued curing<sup>1</sup>; so that it is possible to produce, by subjecting an under-cured vulcanizate to accelerated ageing, a state of cure, as judged by the tensile properties, similar to one produced by further curing, but having a coefficient of vulcanization which in the case of ordinary vulcanization would be taken as indicative of a less advanced state of cure.

In the following table and figure are shown the effect of heating, at 72°, slabs, derived from a given mix, which had been cured at 148° to three different points short of the optimum cure ( $L_{130} = 990$ ). One slab at each cure was tested without heating after five days' rest; two other slabs at each cure were heated at 72° for one and for two days respectively, and were tested one day after removal from the oven. Each slab was sufficient for six rings; so that each of the breaking figures represents the mean of six tests.

TABLE CXV

Sample.	Cured for	"Aged" at 72° for	P <sub>B</sub>	L <sub>B</sub>	L	At P.	Change in Position of Curve in 24 hrs.	Vulcn. coeff.
	Min.	Hrs.						
49I A	70	—	0.695	1146	1207	0.90	—	2.38
B	70	24	0.865	1068	1076	0.90	131	—
C	70	48	0.925	1055	1049	0.90	27	2.30
49I D	90	—	0.95	1105	1141	1.10	—	3.09
E	90	24	1.135	1032	1025	1.10	115	—
F	90	48	1.155	1011	1000	1.10	25	3.22
49I G	110	—	1.29	1050	1052	1.30	—	3.96
H	110	24	1.42	996	976	1.30	76	—
I	110	48	1.46	977	951	1.30	25	4.16

<sup>1</sup> The observation that, as judged by the tensile properties, the vulcanization of rubber can proceed without involving appreciable combination of sulphur with caoutchouc is probably of considerable significance in reference to the theory of vulcanization. In all the investigations which are considered in this section, ageing presents itself, broadly, as involving a change in the properties of the rubber from a mechanical point of view with little or no change in the properties from a chemical point of view.

The results are shown graphically in the following figure.

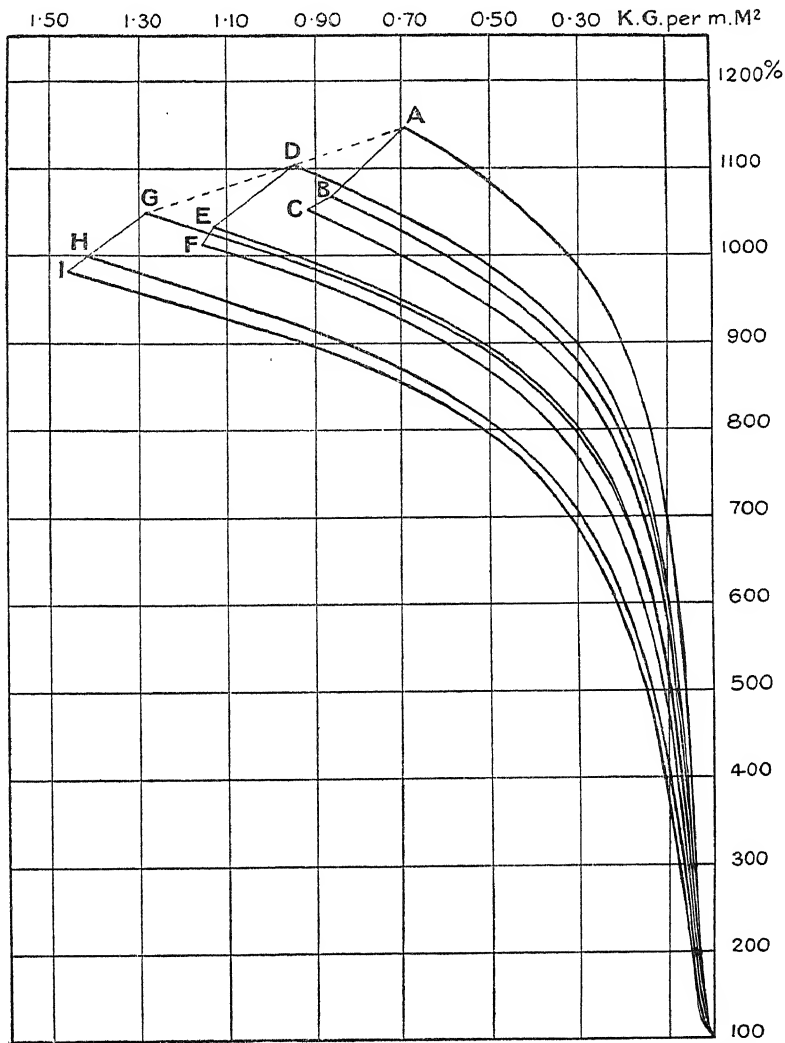


FIG. 35.—Movement of stress-strain curves and breaking points during "accelerated ageing" at 72°.

The dotted line A D G indicates the manner in which the breaking figures change with increasing time of cure at 148°; the lines ABC, DEF, GHI indicate the way in which the breaking

figures change with "accelerated ageing." Twenty-four hours' heating of the product (Sample A) of seventy minutes' curing changes the tensile properties of the vulcanizate so that it gives a curve, O B, approximately coincident with the curve, O D, given by the product of ninety minutes' curing (Sample D). But the coefficient of vulcanization corresponding to O B is only 2.3, whereas the coefficient corresponding to O D is 3.09; and the tensile strength in the product of accelerated ageing is only 0.865 as against 0.95 in the product of continued vulcanization. The "slope" of the curve is not changed during the ageing. The extent of change in the position of the stress-strain curve was less in the second twenty-four hours' heating than in the first.

In some further experiments, heating was continued for longer periods, in order to ascertain whether a position beyond which no further change occurred could be reached. It was found that the change went on continually until the rubber had become too brittle for further tensile tests. The following table shows the results obtained with ten slabs of the above cure A. The temperature of "ageing" was 72°. The breaking figures were obtained from two rings only, and, consequently, run somewhat irregularly. The length at 1.00 kg./mm.<sup>2</sup>, indicating the position of the stress-strain curve, falls continually, although a little irregularly. The change in the coefficient of vulcanization is only slight.

TABLE CXVI

Period of heating at 72° (hrs.)	0	24	48	60	72	84	96	144	216	339
P <sub>B</sub> . . . . .	0.695	0.945	1.01	0.96	0.975	1.03	1.12	1.03	0.85	0.475
L <sub>B</sub> . . . . .	1143	1093	1079	1041	1033	1042	1043	1011	970	754
L <sub>1.00</sub> . . . . .	1227	1106	1076	1048	1038	1034	1020	1005	1001	—
Difference in L <sub>1.00</sub> for 24 hrs. }	—	121	30	56	20	8	28	7.5	1.5	—
Vulcn. coeff. .	2.36	—	—	—	—	—	2.43	—	—	2.58

In a further experiment, observations were made on the effect of heating over a similar extended period at a temperature of 65°. The vulcanizates examined were derived from a single mix, of a different sample of rubber, by curing for three different periods, viz. 70, 90 and 110 minutes. The results obtained were similar to those already described. And, comparing the three cures among themselves, it was seen that similar changes in

the stress-strain curve occurred in the case of a less-cured as in the case of a more-cured vulcanizate: the curve came down the paper continuously. The descent of the curve was more rapid in the case of a less-cured than in the case of a more-cured sample. As regards the breaking figures: the indication was that these moved towards a maximum and then fell; and that the maximum was sharper and higher in the case of a less-cured than in the case of a more-cured sample. (The 70-min. cure had not clearly reached a maximum at the end of its period of heating—384 hours; the 90-min. and the 110-min. cures already showed a marked fall from a maximum after 288 hours' heating.)

The main features of the results are shown in the following table:—

TABLE CXVII

70-min. Cure.				90-min. Cure.				110-min. Cure.			
Period of Heating at 65°.	P <sub>B</sub>	L <sub>0.90</sub>	V.C.	Period of Heating at 65°.	P <sub>B</sub>	L <sub>1.30</sub>	V.C.	Period of Heating at 65°.	P <sub>B</sub>	L <sub>1.30</sub>	V.C.
Hrs.				Hrs.				Hrs.			
0	0.685	1215	1.98	0	0.91	1160	2.82	0	1.285	1050	3.89
24	0.75	1152	—	24	1.03	1098	—	24	1.34	1015	—
48	0.85	1110	—	48	1.10	1073	—	48	1.37	989	—
73	0.92	1076	2.42	72	1.06	1056	3.24	72	1.395	972	4.07
96	0.93	1058	—	96	1.19	1025	—	96	1.365	948	—
144	0.945	1043	2.30	120	1.29	1024	2.96	120	1.41	935	4.02
216	0.95	1012	—	168	1.255	1007	—	168	1.43	925	—
384	0.98	985	2.70	288	1.045	978	3.74	288	1.04	—	4.27

*The stress-strain curve and the breaking-points. Summary.*—The results of de Vries show clearly the insufficiency of a knowledge of breaking-points only in the study of ageing. They show that the whole stress-strain curve should be traced. An inspection of the data shown in Table CXVI (and, also, it may be said, of the data for the 70-min. cure in Table CXVII) will afford an example of the fact that consideration of breaking-points alone without attention being paid to the stress-strain curve as a whole may be misleading. The breaking stresses (P<sub>B</sub>) considered alone would probably be read as indicating that, after the initial rise of the breaking stress, the material had attained a condition of comparative stability in its tensile properties. Yet a consideration of the position of the stress-strain curve, indicated

in the table by  $L_{1.00}$ , shows that the tensile properties of the material are, in fact, changing continually;—at an intermediate load the extension suffered by the material would be quite different at different ageing periods. The conclusions of Stevens as to the comparative stability of cures with vulcanization coefficients in the neighbourhood of 3 (*vide* p. 358 *et seq.*) were based, so far as tensile tests were concerned, on consideration of breaking figures alone. The results of de Vries do not suggest that there is any especially stable state of cure at a vulcanization coefficient in the neighbourhood of 3.

They indicate that samples in a less advanced state of cure (say, vulcanization coefficient = 2) change their tensile properties on "accelerated ageing" in essentially the same manner as samples in a more advanced state of cure (say, vulcanization coefficient = 3 — 4): the position of the stress-strain curve changes in a similar way and even more rapidly; the tensile strength would appear to reach a maximum more slowly, and the maximum in question would—in accord with the previously-mentioned conclusion that the tensile strength corresponding to a given position of the stress-strain curve tends to be lower where it has been brought to its position by accelerated ageing than where it has been brought to its position by continued curing—appear to be lower.

It is to be desired that still more extensive studies of accelerated ageing and of its relation to the state of cure, to the composition of the mix, and to non-accelerated ageing will be undertaken.

#### AGEING, THE OPTIMUM CURE AND THE CHOICE OF AN EVALUATION MIX

The question of the bearing of ageing on the definition of the optimum cure and on the choice of a suitable mix for the purpose of evaluating samples of raw rubber demands some discussion. It has appeared that vulcanizates derived from rubber-sulphur mixes containing such proportions of sulphur as 10 or 7.5 per cent. are unstable, and, when representing cures as advanced as those showing the maximal tensile strength, tend to become, with comparative rapidity, brittle. It should not, however, be concluded from this that, in view of the fact that the greatest attainable stability of state of cure is a prime requirement in the technical employment of rubber, such mixes are unsuitable for the purpose of evaluation, or that, for such a purpose, the

optimum cure is not suitably regarded as the cure giving the maximal tensile strength.

Clearly, in view of its instability, the cure giving, in the case of such mixes, the maximal tensile strength, cannot be regarded as a satisfactory cure from a technical point of view or as a "perfect" cure in any full sense of the term. And some writers<sup>1</sup> have, in consequence, been inclined to attach little importance to the position of maximal tensile strength, and to consider that a less advanced state of cure should be regarded as the optimum cure. Such a view would, however, appear to miss the significance of the position of maximal tensile strength (or of a standard curve in its neighbourhood) as a sharply-defined point of reference for the purpose of the comparative evaluation of raw rubber samples.

Certainly a "correct," "perfect" or "optimum" cure in the full sense of these terms should show the greatest attainable stability. But it should also show, for given constituents of the mix, maximal mechanical properties. To secure an optimum cure in this full sense of the term calls for adjustment, not only of the curing conditions (temperature and duration), but also of the proportions in which the constituents are mixed. And it may fairly be pointed out that, in the case of a rubber-sulphur mix containing as much as 10 or 7.5 per cent. of sulphur there would appear to be no such thing as an optimum or perfect cure in the full sense just indicated. In order to secure from rubber and sulphur only, an optimum cure in the above sense, *i. e.* a product the mechanical properties of which are both maximal and stable, it would be necessary, so far as can be judged by investigations hitherto published, to mix with the rubber a smaller proportion of sulphur than the proportions just mentioned. Yet a mix containing such a smaller proportion of sulphur would not be suitable for the evaluation of raw rubber samples, as it would not show a sufficiently sharp maximum in a series of progressive cures.

*Low percentage of sulphur and stability of tensile properties.* Adverting to the discussion given earlier (p. 325 *et seq.*) on the sharpness of the maximum of tensile strength in a series of progressive cures of rubber-sulphur mixes containing different proportions of sulphur: it may be gathered that a mix con-

<sup>1</sup> Particularly Stevens (various papers). Also the Delft Institute (cf. van Rossem, "Bijdrage tot de kennis van het vulcanisatieproces," 1916, p. 150; *Delft Communics.*, p. 160) and Gottlob (*Gummi-Ztg.*, 1916, 30, 303, 326).

taining a proportion of sulphur in the neighbourhood of 5 per cent. yields at the cure showing maximal tensile strength a product, which in regard to the magnitude of its tensile strength is not appreciably inferior to the maximal tensile strength of a product obtained from the same rubber by means of a larger proportion of sulphur, and which, unlike the latter product, is comparatively stable.

From Table XCVII (p. 330) it may be seen that rubber sample No. 452, when mixed with 5 per cent. of sulphur, gave maximal breaking figures, at a cure of 120 minutes, of  $P_B = 1.35$ ,  $L_B = 1124$ ,  $P_B \times L_B/100 = 15.17$  kg./mm.<sup>2</sup>; and when mixed with 7.5 per cent. of sulphur gave maximal breaking figures, at a cure of 75 minutes (optimum cure = 80 min.), of  $P_B = 1.33$ ,  $L_B = 1011$ ,  $P_B \times L_B/100 = 13.45$  kg./mm.<sup>2</sup> The fact that the ultimate elongation is greater in the case of mixes containing less than in the case of corresponding cures of mixes containing more sulphur has the result in the present case of making the tensile product,  $P_B \times L_B$ , *i. e.* the breaking stress referred to the actual cross section at break, better in the former case than in the latter; although the breaking stress,  $P_B$ , referred to the original cross section is substantially the same in the two cases.<sup>1</sup>

It is probable that the cure giving the maximal tensile strength in the case of the 5 per cent. mix would "age" much better than that giving the maximal tensile strength in the case of the 7.5 per cent. mix. In the former case almost all the sulphur present is combined (vulcanization coefficient = 4.41), whereas in the latter case much free sulphur is present (vulcanization coefficient not determined, but may be assumed to be *ca.* 5). And both general experience in the manufacture of rubber goods and experimental work indicate that the presence of a considerable amount of free sulphur in a vulcanizate is conducive to instability.

<sup>1</sup> Similar relations are to be seen in Eaton's data for mixes of a given sample of raw rubber cured with different proportions of sulphur. (*Dept. Agric. F.M.S., Bull. No. 27, 1918, 115 et seq.*) Thus, at the cure giving the maximal tensile product, mixes (from slab rubber) containing 10, 9, 7 and 4.8 per cent. of sulphur show increasing elongation at break;  $L_B$  being in the case of the four proportions of sulphur mentioned 968, 1006, 1039 and 1157 respectively. The mixes show substantially the same maximal value for the tensile product, the figure being 15.19, 15.09, 15.58 and 15.38 respectively. In the case of these samples the tensile product for the mix containing the smallest proportion of sulphur, *viz.* 4.8 per cent. is not, as in the case to which Table XCVII refers, actually greater than for the mixes containing higher proportions of sulphur. Possibly this difference may be due in part to the fact that the vulcanizing temperature in question (140°) is lower in the present case, and, therefore, the period of exposure of the rubber to a high temperature longer.

In addition to this general consideration based on the proportion of free sulphur present, further support for the assumption that the vulcanizate showing maximal tensile strength for a 5-per cent. mix would age well may be seen in the effect on the tensile properties of the prolongation of the curing period. Prolongation of the curing period may not unfairly be viewed in the present connection as the subjection of the vulcanizate to ultra-accelerated ageing.

An inspection of the data in Table XCVII and Fig. 30 (p. 331) shows that, while in the case of the 7.5-per cent. mix continued curing, beyond the point giving the maximal tensile strength, brings the rubber comparatively quickly into a condition of brittleness, and causes the stress-strain curve to descend the paper rapidly, in the case of the 5 per cent. mix it brings about only small changes in the tensile strength and in the position of the stress-strain curve. The same condition of affairs may be read in the results depicted in Fig. 31 (p. 335). For example: Mixes A and C consist of the same sample of (slab) rubber with respectively 10 and 4.8 per cent. of sulphur. In the former mix the rubber shows its maximal tensile product (15.19) at a cure of 1.5 hours; and a further period of half-an-hour's heating at 140° has, as it were, "aged" the vulcanizate so rapidly that the tensile product has fallen to a figure (11.94) which shows that the material has become brittle. In the latter mix, on the other hand, the rubber shows its maximal tensile product (15.38) at a cure of three hours; and a further period of two hours' heating at 140° has, as it were, "aged" the vulcanizate so little that the value of the tensile product has fallen only a little (to 14.49). The influence of a continuation of the curing beyond the point giving the maximal tensile strength is well shown by the stress-strain diagrams (Fig. 36, p. 384). While the curve for the 10 per cent. mix (146A) changes its position to a great extent during half-an-hour's curing beyond one and a half hours, the curve for the 4.8 per cent. mix (146C) changes its position only slightly during two hours' curing beyond three hours.

*Low percentage of sulphur and the sharpness of the tensile maximum.*—While, then, a comparatively small proportion of sulphur (say, 5 per cent.) in a rubber-sulphur mix would, it may be presumed, when the mix was cured to the position of maximal tensile strength, lead to a comparatively stable product, it would not be a suitable proportion for discriminating sharply



between samples of raw rubber in regard to their vulcanizing properties, because it would lead to a lack of sensitiveness in the mix. The insensitive character, on the one hand, of a

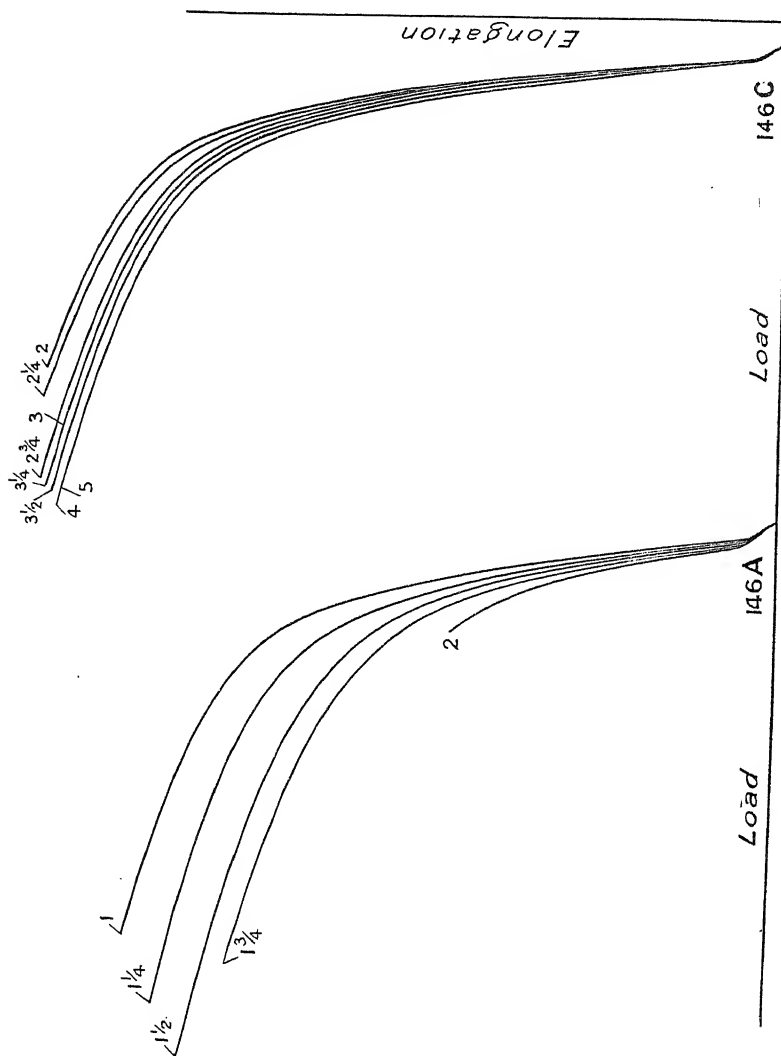


FIG. 36.

rubber-sulphur mix containing a comparatively small proportion of sulphur, and the sensitive character, on the other hand, of a rubber-sulphur mix containing a comparatively large proportion of sulphur were made apparent in discussion (p. 325)

of the question of the *sharpness* with which a maximum occurs in the tensile strength in a series of progressive cures. The sensitiveness of a rubber-sulphur mix containing 10 or 7.5 per cent. of sulphur was seen in the rapidity with which the tensile properties changed as curing was continued beyond the point at which the tensile strength attained a maximum. The insensitiveness of a rubber-sulphur mix containing 5 per cent. or less of sulphur was seen in the slowness with which the tensile properties changed as curing was continued beyond the point at which the tensile strength first got into the neighbourhood of its maximal value. (Cf. also Fig. 36.) The insensitiveness to prolongation of curing beyond the optimum point shown by a low-sulphur mix may not unjustly be regarded as another aspect of the stability of the vulcanizate, and, conversely, the sensitiveness to prolongation of curing beyond the optimum point shown by a high-sulphur mix as another aspect of its instability. It would not be merely paradoxical to say that a high-sulphur mix is suitable for the discrimination of raw rubber samples just because the vulcanizates from it do not age well.

*Practical value of the comparison of raw rubber samples in a rubber-sulphur mix.*—The place which the comparison of rubber samples in a sensitive mix consisting of rubber and sulphur only may be expected to occupy in relation to the evaluation of rubber for technical purposes may be indicated here. It is reasonable to suppose that the testing of raw rubber in such a mix will provide a means of making a *general* evaluation of the rubber, which will, for most purposes, form the best and most convenient basis for the employment of the rubber in technical mixes. The mixes used technically are very numerous (as many as a thousand may be on record in a given factory) and often complicated. It is manifestly impossible, before employing a sample of rubber, to examine its behaviour in any appreciable number of such mixes; and it would seem desirable that, so far as possible, some fixed basis should be adopted for judging samples of rubber and directing their industrial employment. It should then be possible, with the data provided by comparison on this basis, (a) to pick out a sample of rubber identical with or closely similar to a sample which in the past was found to give satisfactory results, for certain purposes, under certain conditions, (b) when, as a result of systematic investigation, a sufficient store of exact data as to the correlation between behaviour referred to the fixed basis and behaviour under a wide range of technical conditions has been accumulated, to

form a judgment as to suitable uses for a given sample of rubber and to adjust the character of the mix and the conditions of cure for any such purpose when employing the sample in question.

That behaviour in a rubber-sulphur mix containing a comparatively high proportion of sulphur is probably the most suitable basis on which to make a general evaluation of rubber samples is suggested by several considerations, of which two are mentioned here: (1) Owing to its sensitiveness, such a mix allows of samples of raw rubber being distinguished sharply. As will appear in the succeeding chapter, technical mixes are for the most part comparatively insensitive. High-sulphur, rubber-sulphur mixes enable rubber samples to be distinguished not only with greater precision, but also with greater rapidity and convenience than do technical mixes. They do not appear to call for determinations of vulcanization coefficients, whereas, in order to distinguish different states of cure in less sensitive mixes with exactness, determinations of vulcanization coefficients seem often to be demanded. (2) There is the following general consideration pointing to a simple rubber-sulphur mix as the most logical mix in which to make a general comparison of rubbers: the consideration, namely, that in curing such a mix we are dealing with the reaction which forms the basis of all rubber manufacture—the reaction between rubber and sulphur—in its simplest form, unmodified by the presence of other materials.

Confessedly, correlations between the behaviour of rubber samples in an "evaluation mix," such as that here in question, and their behaviour in the numerous types of mix employed for technical purposes have not yet been worked out; and working them out presents a wide field for systematic investigation. (Cf. the following chapter.) It may be that the relation between samples of rubber in different technical mixes is not in all cases parallel with their relation in an "evaluation mix." It may still be found necessary in some cases, in order to determine the suitability of a given sample in a specific technical mix or the mode of its employment for a specific technical purpose, to test it directly in a particular mix or under particular conditions. But, even allowing for this possibility, it is probable that the development of a system of evaluating rubber, on general lines, of such a character that state of cure can be judged by tensile tests only, may justly be conceived as an important aim of technical rubber research.

## CHAPTER XVI

### TECHNICAL MIXES

For technical purposes a simple mix of rubber and sulphur only is seldom used. In the manufacture of almost all rubber goods vulcanized in the hot way, other materials in addition to sulphur are incorporated with the rubber on the mixing rolls. Any extensive consideration of technical mixes would be beyond the scope of the present volume. And, indeed, although a large amount of information of an empirical and traditional character and a good deal of a systematic character is, of course, available in rubber factories, very few systematic investigations have yet been published in relation to technical mixes.<sup>1</sup> As was indicated in the closing paragraph of the preceding chapter, a full, systematic study of progressive vulcanization in technical mixes, particularly in the more important and typical ones, including a study of the stability of the vulcanizates and of the influence of various ingredients, and including correlation of the results with the results obtained in rubber-sulphur mixes, presents itself as one of the tasks immediately ahead for rubber research.

A number of points concerning technical mixes which bear upon the problem of rubber testing will be noticed in what follows.

#### COMPARATIVE INSENSITIVENESS OF MINERALIZED MIXES

Technical mixes are, typically, comparatively insensitive, in the sense that the mechanical properties of the vulcanizates

<sup>1</sup> The manufacture of rubber goods, particularly in respect to the composition of the mixes and the conditions of vulcanization, has been and still is largely marked by a secretive attitude on the part of the manufacturers. It is unnecessary to enlarge upon this circumstance for the purpose of convincing readers of the present volume that such an attitude, particularly in the present state of our scientific knowledge of rubber, is short-sighted and symptomatic of a considerable element of empiricism in the industry. The following recent comment may be noted: "The rubber industry of to-day can learn a profitable lesson from a comparison of present conditions in the iron and steel industry with those of the 'good old days' before the spread of technical knowledge" (Editorial, *Chem. Met. Eng.*, 1919, 20, 611).

produced in a series of progressive cures may change only to a small extent over a considerable range of cures. In illustration of this, the following results, given by Kratz and Flower,<sup>1</sup> may be quoted. A simple type of "mineralized" mix of the following composition, viz. latex crêpe, 100; zinc oxide, 100; sulphur, 5; an amine (accelerator), 0.33 parts, was vulcanized for increasing periods of time at a temperature of 298° F. (50 lbs. steam pressure, 147.7° C.). Zinc oxide is one of the most largely used "mineral" ingredients of technical mixes. The purpose of introducing the amine into the mix was to accelerate curing, for experimental convenience.

It may be remarked here that, as in the case of the above mix, the proportion of sulphur in technical mixes is usually very considerably less than the proportions which have chiefly been the subject of consideration in preceding chapters.

TABLE CXVIII

Time of cure (min.).	Combined sulphur (per cent.).	P <sub>B</sub> lb/in. <sup>2</sup>	L <sub>B</sub>	Sub-permanent set (per cent.).
10	0.404	—	—	—
15	0.578	—	—	—
20	0.663	—	—	—
25	0.840	—	—	—
30	1.080	1527	825	14.32
40	1.330	1533	810	14.06
50	1.490	1920	807	15.23
60	1.690	2277	797	15.62
70	1.875	2015	785	17.97
80	2.170	2102	790	20.30
90	2.485	2055	780	21.09
120	2.945	2156	778	24.22
150	3.410	2060	785	25.78
180	3.600	1725	777	23.44
210	3.780	1558	780	23.44
240	3.920	1435	752	18.75

It will be observed that over the range of cures 70–150 min. (inclusive) the breaking figures show no change greater than the experimental error, although the period of cure is more than doubled and the vulcanization coefficient approximately doubled.

Zinc oxide appears to have little influence on the velocity of combination of sulphur with rubber (cf. p. 392). In the following table are shown results obtained by Fol and van Heurn<sup>2</sup> with

<sup>1</sup> *J. Ind. Eng. Chem.*, 1919, **11**, 30.

<sup>2</sup> *Meded. Delft*, 1916, p. 334.

mixes containing litharge and magnesia, two very frequent constituents of technical mixes, which are recognized as being vulcanization accelerators. Three samples of rubber (Crêpe I, Crêpe II and Fine Hard Para) were mixed with sulphur, litharge and magnesia in the following proportions: 85 parts rubber: 7.5:5:2.5. The mixes were vulcanized for the times indicated at 148° (3.5 atmospheres steam pressure). The period occupied in raising the temperature of the autoclave to the vulcanizing temperature (the "rise") was 4 minutes (1 min., 0-1.5 atmos.; 2 min., rest; 1 min., 1.5-3.5 atmos.). Eight or nine rings at each cure were tested on the Schopper machine. The mean breaking-points are shown in the table.

TABLE CXIX

Period of vulcn. } (min.)		1	5	10	15	20	25	30	40
Crêpe I	P <sub>B</sub> .	1.17	1.18	1.24	1.41	1.44	—	1.49	—
	L <sub>B</sub> .	806	800	803	796	796	—	789	—
	C.S. .	2.05	2.91	3.56	4.96	5.17	—	5.27	—
Crêpe II	P <sub>B</sub> .	0.94	1.01	1.05	1.05, 1.09 <sup>1</sup>	1.10	1.19	1.28	1.32
	L <sub>B</sub> .	758	756	770	757, 752 <sup>1</sup>	733	741	738	704
	C.S. .	1.83	2.26	3.01	3.12	3.76	4.09	4.51	5.26
Fine Hard Para	P <sub>B</sub> .	1.15	1.15	1.11	1.13	1.17	1.22	1.26	—
	L <sub>B</sub> .	811	783	761	767	766	770	780	—
	C.S. .	0.85	1.51	1.94	2.05	2.37	2.91	3.13	—

C.S. = Combined sulphur (per cent.).

An inspection of the above results will show that progressive cures of a mix such as that in question may display only small changes or even practical constancy in tensile properties (so far, at all events, as these are revealed by the breaking-point) over a wide range of cures and vulcanization coefficients.

#### FIXATION OF SULPHUR BY MINERAL CONSTITUENTS

In the case of many technical mixes probably some of the sulphur enters into combination with the inorganic portion of the mix. Ditmar and Thieben<sup>2</sup> record the following experiment: Mixtures of 10 g. of the various commonly-used compounding

<sup>1</sup> This and subsequent figures for this mix were obtained on another sample of it.

<sup>2</sup> *Koll. Zeit.*, 1912, 11, 77.

ingredients shown in the following table with 2 g. of sulphur were heated under typical vulcanizing conditions, viz. in an autoclave for three-quarters of an hour (with ten minutes' "rise") at four atmospheres steam pressure. The products were extracted for one day with acetone; and the sulphur in the extract and in the residue was determined. The results were as follows:—

TABLE CXX

Compounding ingredient	MgCO <sub>3</sub>	MgO	ZnO	BaSO <sub>4</sub>	PbO	CaCO <sub>3</sub>
Sulphur (per cent.) fixed by ingredient	7.2	80.5	73.6	62.33	66.06	76.20

In the case of each of the above substances the formation of sulphate and of sulphide was observed.<sup>1</sup> The analytical problem of distinguishing between the sulphur inorganically combined and that combined with the rubber in vulcanizates produced from mixes containing inorganic constituents capable of reacting with sulphur has not been solved fully. In Table CXIX the sulphur in combination is expressed, not as a percentage of the rubber present (the vulcanization coefficient), but as a percentage of the whole minus the sulphur. This was done because of the difficulty of distinguishing analytically between that portion of the combined sulphur held by the rubber and that portion of it in combination with the inorganic part of the mix.

Fol and van Heurn, working with vulcanizates from a mix consisting of plantation crêpe, zinc oxide, magnesium oxide and sulphur in the proportions 38.5 : 47.7 : 10 : 3.8, were not able to obtain consistent results when they attempted to arrive at values for the sulphur in combination with the rubber by determining the total combined sulphur, and the sulphur in combination with the inorganic constituents and subtracting the latter from the former. Stevens<sup>2</sup> has published a method for determining sulphur present in vulcanizates as sulphide and sulphate. The rubber is swollen in a solvent, such as ether, and is warmed with a little hydrochloric acid; the hydrogen sulphide evolved being collected in lead acetate. The material is then treated thoroughly with strong hydrochloric acid in order to extract the sulphate.

<sup>1</sup> Lime showed a greater degree of change than any of the above substances; and the acetone used in this case for extraction became transformed into a liquid, with an unpleasant smell, which first distilled over at 163°.

<sup>2</sup> *Analyst*, 1915, 40, 275.

## ACTIVE AND PASSIVE COMPOUNDING INGREDIENTS

It has already been mentioned that some of the constituents used in technical mixes accelerate the vulcanization, while others affect the rate of vulcanization little or not at all. Examples of the latter class, which may be known as "indifferent fillers," are to be seen in the following table, which shows the result of an experiment recorded by the Delft Institute.<sup>1</sup>

TABLE CXXI

*Mixes of 100 g. latex crêpe and 7.5 g. sulphur, with additions noted, vulcanized under identical conditions*

	Vulcanization coefficient.
None	2.4
25 g. flint powder (evenly mixed while cooling)	2.5
" " " (added in 4 parts while cooling, with one day interval between each addition)	2.6
25 g. pumice powder (evenly mixed while cooling)	2.8

Ditmar and Thieben<sup>2</sup> suggest that materials which are chemically indifferent to sulphur may yet noticeably accelerate the combination of sulphur with caoutchouc by increasing the degree of dispersion of the rubber.<sup>3</sup> But the data which they offer in illustration of this suggestion do not seem very convincing.<sup>4</sup>

Beadle and Stevens<sup>5</sup> made some experiments on the effect of mixing zinc oxide with rubber and sulphur which indicate that, although zinc oxide has a marked effect on the tensile properties of the vulcanizate, it has very little influence on the combination of sulphur with rubber. A similar conclusion was indicated in the case of talc. Mixes, containing 100 parts of

<sup>1</sup> *Meded. Delft*, 1916, p. 107; *Delft Communics.*, p. 200.

<sup>2</sup> *Koll. Zeit.*, 1912, 11, 77.

<sup>3</sup> They say, speaking with reference to the indifferent filler talc (cf. Beadle and Stevens' experiments, *infra*): "Diese Wirkung kann man also lediglich nur auf eine starke Dispersion zurückführen, welche Talkum in Suspension im Kautschukkolloid bewirkt. Diese Dispersion steigt immer mehr, je grösser die Menge des Zugesezten Talkes wird."

<sup>4</sup> It may be mentioned that the state of sub-division of indifferent fillers added to rubber, although so far as available data goes without significance in regard to the velocity of the reaction between rubber and sulphur, appears to be of great significance in regard to the physical properties of the vulcanized product (cf., *e.g.*, p. 500). This is an aspect of rubber technology which has not yet been fully explored.

Wiegand (Paper read before Society of Chemical Industry, Montreal, 1919) draws some interesting comparisons between inorganic fillers in rubber mixes and pigments in paints, particularly as regards the influence of the fineness of state of sub-division on (a) the quantity of the material "taken up" by plastic rubber and its hiding power in a paint, (b) the stability of rubber cements and of paints.

<sup>5</sup> *J. Soc. Chem. Ind.*, 1911, 30, 1421.



rubber, 5 parts of sulphur, and, in addition, the amounts of zinc oxide and of talc noted in the following table, were vulcanized under uniform conditions. In the absence of both zinc oxide and talc, the percentage of combined sulphur<sup>1</sup> was 2.42 in the case of Sample I and 2.40 in the case of Sample II.

TABLE CXXII

Parts of zinc oxide or talc	.	0.5	2	5	15	40	75
Combined sulphur in case of ZnO	:	2.68	2.68	2.73	2.75	2.80	2.81
" " " talc	:	2.56	2.55	2.62	2.53	2.69	2.60

Van Heurn,<sup>2</sup> in two experiments only, found zinc oxide to have a small retarding effect on the combination of sulphur. Mixes containing 92.5 parts of the same rubber and 7.5 parts of sulphur were vulcanized with and without the addition of 1 part of zinc oxide. Without zinc oxide, the vulcanization coefficients found in two experiments were 3.11 and 3.16; with zinc oxide, 2.75 and 2.70.

*Litharge and magnesia.*—Litharge, magnesia (MgO) and lime are inorganic substances, widely employed in technical mixes, which are recognized as being vulcanization accelerators. The marked accelerating effect of even small amounts of magnesia, as compared with the almost entire lack of accelerating effect of even large amounts of zinc oxide on the rate of combination of sulphur with rubber may be seen in the following results of Beadle and Stevens,<sup>3</sup> which form an extension of the results given in the preceding table.

TABLE CXXIII

Composition of the mix (in parts).				Combined sulphur (per cent.).
Rubber.	Sulphur.	Zinc oxide.	Magnesia.	
100	5	—	—	2.41
60	3	37	—	2.75
60	3	36	1	4.37
60	3	35	2	4.77
60	3	34	3	4.83

The accelerating effect of magnesia and of lime may be seen in the reduction which their presence brings about in the time of optimum cure in Table CVI.

The mode of action of litharge—probably the most widely used inorganic accelerator—has been the subject of an investiga-

<sup>1</sup> Calculated as (total sulphur — free sulphur) ; expressed as a percentage of the rubber present.

<sup>2</sup> *Meded. Delft*, 1916, p. 110; *Delft Communics.*, p. 202.    <sup>3</sup> *Loc. cit.*

tion by Seidl,<sup>1</sup> who concluded that the accelerating effect of litharge was due to the heat produced by reaction between the litharge and small quantities of hydrogen sulphide arising from action of the sulphur on the resin and other components associated with the caoutchouc hydrocarbon. Seidl concluded from calorimetric observations that the temperature of a rubber-sulphur mix containing litharge was higher than that of a corresponding mix containing, say, zinc oxide instead of litharge, and even higher than the temperature of the vulcanizing press in which the curing was done. He considered that the heat evolved by the reaction between litharge and sulphur, according to the equation  $4\text{PbO} + 4\text{S} = 3\text{PbS} + \text{PbSO}_4$ , was insufficient to explain the temperature of a rubber-sulphur mix containing litharge. He concluded that the heat evolved by the reaction between litharge and hydrogen sulphide, with the formation of lead sulphide and water, would be sufficient to explain the phenomenon. The hydrogen sulphide necessary for this reaction, he considered, was derived from the action of sulphur on the resins or other materials accompanying the caoutchouc. The resin from Para rubber and sulphur, when heated together in a calorimeter, produced a very marked rise in temperature over the temperature of the surrounding oil-bath. Further, when mixes of (a) untreated Para rubber, (b) the same deresinated, (c) the same purified (by extraction with acetone, dissolution in petroleum ether, and precipitation with alcohol) with, in each case, litharge and sulphur were vulcanized in a calorimeter, (a) showed a higher rise in temperature than (b); and (b) than (a). The percentages of combined sulphur after thirty minutes' cure in a press at three atmospheres were—(1) 2.425, (2) 1.730, (3) not recorded.

*Comparison of inorganic and organic accelerators.*—Some comparisons have been published of the relative effectiveness and influence on the properties of the product of inorganic and organic accelerators, although the subject has not yet been studied exhaustively.

Van Heurn<sup>2</sup> found 1 per cent. of magnesia to lead to a higher vulcanization coefficient than 1 per cent. of litharge in a mix of rubber 92.5 : sulphur 7.5 vulcanized at 147° for 1.5 hours. The coefficients in two experiments were as follows: no accelerator : 3.11, 3.16; MgO : 6.90, 6.80; PbO : 4.65, 4.35. In the

<sup>1</sup> *Gummi-Ztg.*, 1911, 25, 710, 748. Cf. Esch and Auerbach, *Gummi-Markt*, 1911, p. 123.

<sup>2</sup> *Meded. Delft*, 1916, p. 110; *Delft Communics.*, p. 202.

case of certain organic accelerators 0.25 per cent. showed a greater effect in promoting the combination of sulphur in a mix (with, however, another rubber sample) of the same composition cured under the same conditions than did the two inorganic accelerators mentioned. The coefficients in two experiments were as follows: no accelerator: 2.46, 2.31; *p*-nitrosodimethylaniline: 8.04, 7.90; piperidine: 7.00, 6.95.

Stevens<sup>1</sup> has compared the effects of increasing small amounts of inorganic and of organic accelerators on the coefficient of vulcanization and on the position of the stress-strain curve in the case of a 90/10 rubber-sulphur mix vulcanized under fixed conditions (1 hour at 138°). He found (a) magnesia in small amounts to be very much more active than litharge in promoting the combination of sulphur; (b) the curve relating the vulcanization coefficient ( $y$ ) to the amount of accelerator ( $x$ ) to be concave to the  $x$  axis in the case of magnesia and convex in the case of litharge, indicating that in larger amounts the differences between the effect of the two accelerators would diminish; (c) magnesia in amount up to 0.6 per cent. to be more active in promoting the combination of sulphur than *isonitrosodimethylaniline*; (d) the curve relating vulcanization coefficient and amount of accelerator to be a straight line for the latter accelerator within the limits taken. He also found the position of the stress-strain curve at a point  $L = 900$  to be (a) much higher in the case of litharge than with the two other accelerators, (b) to be lower with proportions of magnesia up to 0.6 per cent. than with the same proportions of *isonitrosodimethylaniline*. The curves relating the position of the stress-strain curve to the amount of accelerator had, broadly speaking, a similar aspect to that of the curves relating the vulcanization coefficients to the amount of accelerator. The numerical results were as follows:—

TABLE CXXIV

	Litharge.					Magnesia. <sup>2</sup>					<i>Isonitrosodimethylaniline</i> .				
Accelerator (per cent.)	<i>nil</i>	0.1	0.25	0.52	0.8	<i>nil</i>	0.1	0.25	0.4	0.75	<i>nil</i>	0.091	0.182	0.364	0.726
Combined sulphur (per cent.) <sup>3</sup>	1.26	1.25	1.27	1.37	1.75	1.40	2.66	3.31	3.68	4.08	1.40	1.90	2.27	2.97	4.24
P at $L = 900$	0.237	0.244	0.248	0.282	0.370	0.152	0.390	0.755	1.12	1.32	0.152	0.32	0.43	0.827	1.675

<sup>1</sup> *J. Soc. Chem. Ind.*, 1918, **37**, 156 T.

<sup>2</sup> Cf. footnote, p. 395.

<sup>3</sup> Determined after forty hours' extraction with acetone, except in the case of litharge, where the extracted material was treated with HCl in ether before the sulphur was determined.

Kratz and Flower,<sup>1</sup> working under the same conditions as Stevens, *i. e.* with a 90/10 rubber-sulphur mix cured for 1 hour at 35 lb. steam pressure, find magnesia to be less active in promoting the combination of sulphur than an organic accelerator, consisting of a condensation product (unidentified) of an amine and formaldehyde.<sup>2</sup> They found that, when the amount of accelerator was 0.75 per cent. or more, the stress-strain curve at the point  $L = 900$  was lower with magnesia than with the organic accelerator; but they concluded that the tensile properties of rubber-sulphur mixes to which inorganic and of such mixes to which organic accelerators have been added cannot fairly be judged by determining the load required to produce a given length,<sup>3</sup> and that, if breaking figures are determined, the vulcanizates produced from mixes containing the organic accelerator are seen to be markedly superior to those produced from mixes containing magnesia, both as regards tensile strength and

<sup>1</sup> *Chem. Met. Eng.*, 1919, 20, April 15th.

<sup>2</sup> Kratz and Flower used a heavy calcined magnesia; Stevens (*supra*) used a light calcined magnesia. Stevens (*I.R.J.*, 1919, September 20th, p. 527) has pursued the question of the difference in behaviour which is here indicated between different grades of magnesia. He finds that a light grade of magnesia may be a more powerful accelerator than a heavy grade. Presumably the effectiveness of different grades of an inorganic accelerator such as magnesia is partly dependent upon the state of subdivision of the material.

<sup>3</sup> The following notes may be added concerning the attempted comparison of the tensile properties of vulcanizates derived from mixes of different compositions by determining the load corresponding to a given, fixed length, *i. e.* by defining one point of the stress-strain curve. (a) The character of the stress-strain curve appears to differ with differences in the composition of the mix. The relative position of stress-strain curves can fairly be ascertained by defining one point, only if the curves are of the same character. But the addition of inorganic substances appears to modify the form of the curve very considerably (cf. Fig. 37, p. 400). (b) As was emphasized in an earlier chapter, the position of the stress-strain curve has important significance in the comparison of rubbers only with explicit or implicit reference to the position of the stress-strain at the optimum cure. Now, the addition to rubber of even small amounts appears to modify greatly the position of the curve representing the optimum cure.

It should be remarked that not only, as Kratz and Flower conclude, is the determination of the load corresponding to a given fixed length an insufficient basis for the comparison of vulcanizates such as those here in question, but that the determination of breaking figures alone [the basis used by Kratz and Flower] or in conjunction with the determination of the load at a fixed length is also an insufficient basis; although, it may be admitted, it appears to give a juster comparison of the tensile properties of the vulcanizates in the present instance than does the determination of the load at a fixed length. A complete comparison of the effect of inorganic and organic accelerators on tensile properties appears to call for tracing the whole stress-strain curve over a range of progressive cures with each mix.

elongation; and particularly as regards the latter. The data are shown in the following table.

TABLE CXXV

Accelerator (per cent.) . . .		0	0.10	0.25	0.50	0.75	1.00	1.25
Heavy calcined magnesia	{ Combined sulphur (per cent.)	0.684	1.012	1.287	1.500	1.873	1.724	1.821
	{ P at L = 900 . . .	0.163	—	0.501	0.633	0.832	0.886	0.883
	{ Pb . . . . .	0.181	0.564	0.774	0.766	0.914	0.914	1.002
	{ Li . . . . .	1.062	1.037	1.050	1.012	1.000	1.012	1.028
The organic accelerator	{ Combined sulphur (per cent.)	0.684	1.202	1.609	2.079	2.347	2.518	3.004
	{ P at L = 900 . . .	0.163	0.402	0.630	0.678	0.664	0.636	0.642
	{ Pb . . . . .	0.181	0.621	0.871*	1.153*	1.170*	1.250*	1.254
	{ Li . . . . .	1.062	1.025	1.000*	1.075*	1.125*	1.137*	1.187

\* These samples were pinched through by the clamps of the (Scott) testing machine before the point of rupture. Hence the figures are too low.

Eaton and Grantham,<sup>1</sup> in a comparison of a rapid-curing rubber (slab) and a slow-curing rubber (latex crêpe) in two mineralized mixes, of similar composition, except that one contained magnesia and the other litharge, found that the difference in state of cure at a given period of vulcanization between the rapid- and the slow-curing rubber was diminished in the presence of litharge to a greater extent than in the presence of magnesia. (Composition of the mixes: rubber, 60.6; sulphur, 3.0; zinc oxide, 32.3; litharge or magnesia, 4.0 per cent. Temperature of vulcanization, 140°.) Stevens<sup>2</sup> believes that the results are not to be read as showing that litharge is a more powerful accelerator than magnesia, and suggests that the explanation of the phenomena observed by Eaton and Grantham is to be sought in a reduction of the amount of sulphur available for reaction with the rubber on account of a part of the sulphur entering into reaction with the litharge. It is not, however, clear that this explanation is sufficient. And the results of Eaton and Grantham, so far as they go (their primary object was not to compare the potency of different accelerators), should, it would seem, be regarded as exhibiting litharge, when present to the extent of 4 per cent. in a mix such as that mentioned above, as a more powerful accelerator than magnesia.<sup>3</sup>

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 1046.

<sup>2</sup> *Ibid.*, 1918, **37**, 157.

<sup>3</sup> In Eaton and Grantham's investigation, vulcanization coefficients were not determined. The curing periods employed in the investigation, viz. 1, 1.75, 2.25, 2.75 hours, were not adapted to the comparison of the accelerators in question in the case of the rapid-curing rubber; for even at the shortest period curing with this rubber appears to have reached

A close examination of the stress-strain curves published by Eaton and Grantham<sup>1</sup> brings out a number of interesting points. One of these is the "reversion" (cf. p. 332) of the curve on prolongation of curing beyond the optimum point.

It will be gathered from the foregoing remarks that the data available on the influence of inorganic accelerators is only slight, and that the question requires further and more exhaustive examination.

In addition to the constituents of technical mixes which have already received mention in the present section, a large number of others are employed, but have not for the most part been dealt with, in regard to their effect on the properties of the vulcanizate, in any published investigations.<sup>2</sup> Among such other

---

its limit. On more prolonged curing, the stress-strain curve for the magnesia-containing mix remains stationary (except that—a careful examination shows—the steep portion appears to become slightly less steep); and the curve for the litharge-containing mix reverts up the paper (cf. p. 332).

A comparison of the mixes of the slow-curing rubber containing the two accelerators in question reveals the following points: (a) the litharge mix reaches its maximal breaking stress earlier than the magnesia mix; having, in fact, already reached it or passed it at the first cure. Thus: in successive cures of 1, 1.75, 2.25 and 2.75 hours  $P_b \times L_b$  was, for litharge:  $1.27 \times 878$ ,  $1.16 \times 886$ ,  $1.09 \times 874$ ,  $0.94 \times 844$ ; for magnesia:  $0.73 \times 874$ ,  $0.95 \times 871$ ,  $0.97 \times 873$ ,  $1.15 \times 886$ . (b) Although Eaton and Grantham, who remark that differences may occur in the types of the curves given by different technical mixes, carefully refrain from comparing the rate of cure in the different mixes in question by comparing the position of the stress-strain curves at a given cure, it may, nevertheless, be noted that the curve for the litharge mix cured for one hour is very considerably lower than the curve for the magnesia mix cured for the same period of time. (c) The litharge mix, even with the slow-curing rubber, appears to be fully cured at one hour, as in subsequent cures the curve "reverts." The magnesia mix does not appear to be fully cured at one hour in the case of the slow-curing rubber, as the curve does not cease to move down the paper until the 1.75-hour cure is reached. (It is then slightly higher than the litharge curve.) On prolongation of the curing, it remains practically stationary, showing only, like the corresponding curve with the rapid-curing rubber, a tendency to become slightly less steep over the "steep" portion.

It may be added that in the case of the mix containing zinc oxide as the only mineral addition (60.6 rubber; 3.0 sulphur; 36.3 zinc oxide) the curves, both with the slow-curing and with the fast-curing rubber, tend to lie above those of the rubbers in the litharge and magnesia mixes; and, further, that the curve for the slow-curing rubber descends continually over the range of cures mentioned, and that the curve for the fast-curing rubber begins to revert slightly.

<sup>1</sup> As shown in *Dept. Agric. F.M.S. Bull.*, No. 27, 1918.

<sup>2</sup> Except for the early investigation of Heinzerling and Pahl (*Mitt. des Vereins zur Beförderung des Gewerbsfleisses*, 1891, 350; 1892, 25. *Proc. Inst. Civ. Eng.*, 1892-3, 111 (1), 505; *J. Soc. Chem. Ind.*, 1892, 11, 536; 1893, 12, 51).

ingredients may be mentioned whiting, barytes, carbon black,<sup>1</sup> lithophone,<sup>2</sup> talc, antimony sulphide, bitumens.

#### CHARACTER OF THE STRESS-STRAIN CURVE WITH TECHNICAL MIXES

The stress-strain curves given by typical technical mixes and their relation to progressive curing have not yet been studied with any closeness. It has already been mentioned (p. 222) that the addition of "compounding ingredients" modifies, in a manner and to a degree dependent upon their nature and amount, the characteristics which distinguish the stress-strain curves of high-grade rubber-sulphur vulcanizates. In general it may perhaps be said that increased "mineralization" tends increasingly to diminish the contrast between the steep and the flat portions of the curve, and, finally, may give the curve a character approximating to the stress-strain curve of rigid materials.

Eaton and Grantham remark in connection with their comparison of slow- and fast-curing rubber in technical mixes (see p. 399) that the character of the curves for such mixes differed considerably according to the composition of the mix (cf. Fig. 37).<sup>4</sup>

Schidrowitz and Goldsbrough<sup>3</sup> state that, while in the case of mixes containing a small proportion of sulphur, together with non-accelerating inorganic ingredients, the stress-strain curve may, as was noted earlier (p. 330) in the case of low-sulphur rubber-sulphur mixes cured to a point at which substantially all the sulphur is in combination, show only a slow "reversion" of the curve up the paper, yet in the case of mixes containing quantities of accelerating inorganic ingredients such as are commonly used in rubber works the change in the stress-strain curve may be very marked indeed: "reversion" may be followed by an increase in "slope," and, finally, the curve may become convex instead of concave to the stress axis, *i. e.* the specific

<sup>1</sup> In recent years considerably employed to replace zinc oxide.

<sup>2</sup> The intimate mixture of zinc sulphide and barium sulphate produced by the mutual precipitation of solutions of zinc sulphate and barium sulphide.

<sup>3</sup> *I.R.J.*, 1919, 57, 269.

<sup>4</sup> The authors remark that in this figure "the curves cross each other in some cases and are not parallel beyond the point of inflexion." It is to be noted, however, that the curves for any one rubber sample (A, B, C, D, on the one hand; E, F, G, H on the other hand) do not cross each other.

character of the rubber curve may disappear, and the curve may assume the character common to rigid materials.

#### VARIATION IN TECHNICAL MIXES

Eaton and Grantham<sup>1</sup> have compared in simple technical mixes samples of rubber, which, when compared in a sensitive rubber-sulphur mix (10 per cent. sulphur in the mix; vulcanization temperature, 140°), showed a wide variation in their rate of cure and in their tensile strength. It was found that in all the mineralized mixes examined the samples showed a variation in their rate of cure in the same direction as, but smaller in degree than in the sensitive rubber-sulphur mix; and also that their maximal tensile strength showed a variation similar to that in the rubber-sulphur mix. The samples of rubber in question were slab rubber and latex crêpe. The mixes contained zinc oxide and either litharge or magnesia. The proportion of sulphur in the mixes was, as is generally the case in technical mixes, small. The mixes were cured over a range of times. The following figure shows on the left hand the stress-strain curves obtained at a single time of cure (2 hours at 140°) for a sample of slab and for a sample of latex crêpe compared in four different mixes. The mixes were as follows:—

*Samples 136*

(Percentages).	Rubber.	Sulphur.	ZnO.	MgO.	PbO.
A and E . . .	60	3	37	—	—
B and F . . .	60	3	35	2	—
C and G . . .	48	3·8	38·5	—	9·6
D and H . . .	93	7	—	—	—

A, B, C, D represent the mixes containing the slab rubber; E, F, G, H the mixes containing the latex crêpe.

An examination of the relative positions of the slab and the crêpe rubber in each pair of mixes shows (a) that in each case the mix containing the slab rubber is, as shown by the lower position of the stress-strain curve, in a more advanced state of cure than the corresponding mix containing the crêpe rubber, but that (b) the difference in the state of cure of the mix containing the slab rubber and the mix containing the crêpe rubber is smaller in the case of the mineralized mixes (A and E, B and

<sup>1</sup> *J. Soc. Chem. Ind.*, 1916, **35**, 1046.



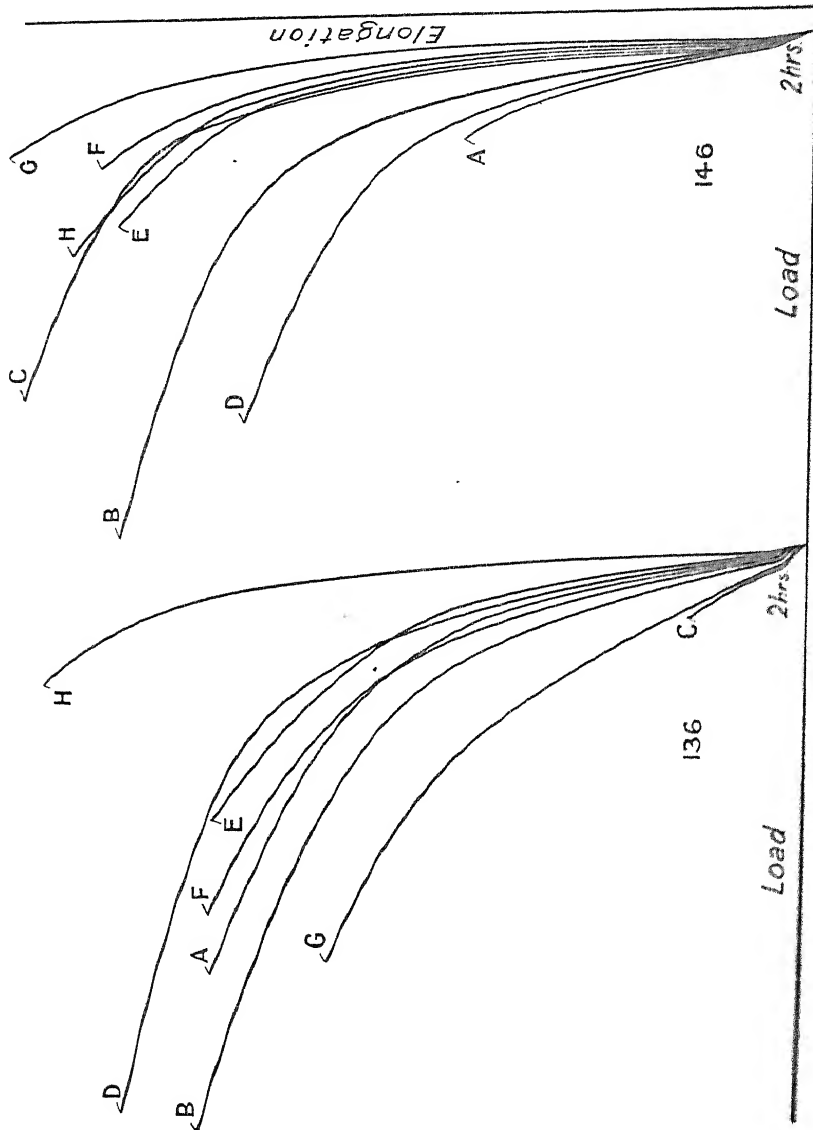


FIG. 37.

F, C and G) than in the case of the rubber-sulphur mix (D and H).

Eaton and Grantham found that the difference in position of the stress-strain curves for the mineralized mixes containing slab and corresponding mixes containing crêpe in general became less distinct as the period of curing was prolonged, and tended to disappear. This they attributed to the whole of the small proportion of sulphur having entered into combination in the more rapid-curing mix of each pair at an earlier time than in the less rapidly curing mix.<sup>1</sup> As already mentioned, prolongation of curing had in several cases the effect of causing the stress-strain curve to move up the paper—to "revert" slightly.

Eaton and Grantham found the accelerator litharge, in the proportions used (4.0 — 9.4 per cent.), to obscure the variation in the rate of cure of raw rubber samples to a greater extent than either magnesia or zinc oxide.

Included in Fig. 27 is a set of curves (146) showing the result of comparing a fast- and a slow-curing rubber (slab and crêpe) in rubber-sulphur mixes with different proportions of sulphur. Mixes A and E contained 10; D and H, 9.1; B and F, 17.0; C and G, 4.8 per cent. of sulphur. As in the case of samples 136, A, B, C and D contained the fast-curing; E, F, G and H the slow-curing rubber.

<sup>1</sup> Determinations of the amount of combined sulphur were not made. While it is not improbably true that in the case of Eaton and Grantham's mixes the practical lack of change in the tensile properties over a wide range of cures is associated with complete combination of sulphur, it should be noted that the results of Kratz and Flower and of Fol and van Heurn, quoted earlier (pp. 388-9), show that lack of change in the tensile properties, at all events as regards breaking figures, of mineralized mixes over a wide range of cures may not be associated with complete combination of sulphur.

## CHAPTER XVII

### VISCOSITY DETERMINATIONS

THE hope was entertained that the determination of the viscosity of raw rubber samples dissolved in a suitable solvent would supply a simple means of evaluation, which would render vulcanization tests unnecessary, at least for certain purposes. This hope was based on the apprehension that the vulcanizing properties of a rubber must be dependent fundamentally on the degree of aggregation<sup>1</sup> of the caoutchouc.<sup>2</sup> The hope has not been realized. It has not been found that the viscosity is a sufficiently reliable index to vulcanizing quality to allow of its use for the evaluation of raw rubber. The degree of correlation between viscosity and vulcanizing qualities is, however, sufficiently considerable to make it not impossible that, at some future date, when all the various factors concerned with the raw rubber which influence the result of vulcanization have been more clearly distinguished, viscosity determinations may be found to be of practical value as an index to certain fundamental characters in raw rubber samples. To say that, while in our present state of knowledge concerning especially the more intimate characters in raw rubber which determine vulcanizing quality and concerning the nature of vulcanization, the apprehension of which mention was made is without immediate practical bearing, yet that nothing has transpired to disprove its general soundness and to make the

<sup>1</sup> And, if there are differences in the degree of polymerization in raw rubber samples, on the degree of polymerization.

<sup>2</sup> The matter is poised by Schidrowitz (*Rubber*, 1911, 156) as follows:—  
“The extension—by applying a load—of a piece of solid rubber is in its general mechanical aspects very similar to the non-turbulent flow of a liquid through a narrow conductor. The effect of extension is attained mainly by overcoming the internal friction produced by the rubber molecules or aggregates passing one another. It is well known that the viscosity of a liquid, or of a solid contained in a liquid, connotes a state of aggregation, of molecular complexity or of physical aggregation, as the case may be. Considering these facts jointly, it appears more than probable that viscosity measurements of rubber solutions must furnish valuable information regarding the physical or chemical state of aggregation of the rubber substance, and that the result of such measurements, made under proper conditions and properly interpreted, must be intimately connected with the strength or “nerve” of the dissolved material.”

hope vain that it may in the future prove to have at least a limited practical bearing, would probably be to state the case judicially.

#### DETERMINATION OF VISCOSITY

Attention was first directed to the question of the possibility of employing viscosity determinations for the evaluation of raw rubber by Schidrowitz and Goldsbrough.<sup>1</sup> A large amount of work on the technique of the measurement of the viscosity of rubber solutions has been performed, particularly by Schidrowitz and Goldsbrough, by Fol,<sup>2</sup> by van Heurn,<sup>3</sup> by van Rosem<sup>4</sup> and by Gorter;<sup>5</sup> and extensive surveys of the relation between viscosity and vulcanizing properties have been made by van Rossem<sup>6</sup> and de Vries.<sup>7</sup> The measurements have usually been made in benzene solution.<sup>8</sup> The viscosometer employed most extensively has been a simple Ostwald double-bulb instrument of specified dimensions,<sup>9</sup> but other types of instrument have also been employed.<sup>10</sup> The temperature of observation generally adopted has been 30°, *i. e.*, a temperature convenient for work in the tropics.

The solutions employed have usually contained an amount of rubber in the neighbourhood of one per cent. or less. Van Heurn showed that shaking can be used, in order to expedite the preparation of the solution, without affecting the value for the viscosity. Stevens<sup>11</sup> showed that by fractionally dissolving rubber in benzene differences in viscosity, which he attributed to a diminishing proportion of resin in successive fractions, were exhibited by different fractions. Van Heurn has confirmed the conclusion that an initial fraction shows a lower viscosity than a later one; but has concluded that, if care is taken to dissolve the greater part of the rubber—say, 90 per cent.—when preparing a solution for viscosity

<sup>1</sup> *J. Soc. Chem. Ind.*, 1909, 3. Alexrod (*Gummi-Ztg.*, 1905, 19, 1053; 20, 105) had earlier made some viscosity measurements with rubber solutions with a different aim in view. Cf. also Henri (Morisse, *Le Latex*, Paris, 1908, p. 407).

<sup>2</sup> *Meded. Delft*, 1912, p. 22; *Koll. Ziet.*, 1913, 12, 131.

<sup>3</sup> *Ibid.*, 1916, pp. 357, 397, 423.

<sup>4</sup> "Bijdrage tot de kennis van het vulcanisatieproces," Amsterdam, 1916.

<sup>5</sup> *Meded. over rubber*, No. IV (1915).

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Archief*, 1918, 2, 456.

<sup>8</sup> For measurements in other solvents, see Kirchhof (*Koll. Zeit.*, 1914, 15, 30) and Hellendoorn (*Meded. Delft*, 1916, p. 470; *Delft Communics.*, p. 92).

<sup>9</sup> Cf. Schidrowitz and Goldsbrough, *loc. cit.*; Fol, *loc. cit.*

<sup>10</sup> Alexrod's apparatus and the modification of it described by Frank (*Gummi-Ztg.*, 1911, 25, 990) have the defect that the flow is turbulent. Gorter's apparatus is a simple one in the form of a pipette. It would appear to be unsuitable for exact work.

<sup>11</sup> *I.J.R.*, 1913, 46, 345.

measurements, the result is not likely, in most cases, to differ seriously from that obtained after complete solution.

Fol and, later, Kirchhof<sup>1</sup> observed that, on taking a second reading of the time of flow of a given solution in a viscometer, the time was less than at a first reading. The explanation of this was found by van Heurn to lie in the influence of light on the viscosity. If the readings were taken in the dark, there was no difference between successive readings. In practice it was found best to take readings in the light and accept the first one; using a second reading simply for the purpose of making certain that there was no gross error in the first.

Van Heurn, who, like others, found the viscosity of rubber to be greatly reduced by working on the rolls, investigated the question as to whether the admixture with rubber in a plastic condition of materials commonly used in rubber mixes—in his experiments, sulphur, magnesia and litharge—affected the measurement of the viscosity of the rubber. He found that, if allowance was made for the amount of sulphur entering into solution, the value of the viscosity for a sample of rubber, which had been rendered plastic, as obtained from a “dough” containing other ingredients, agreed with the value obtained in the absence of other ingredients.

*Method of expressing viscosity numerically.*—There has been a good deal of discussion as to the most suitable method of expressing viscosity in the case of rubber. Schidrowitz<sup>2</sup> drew a curve through the value of the viscosities, relative to the viscosity of the solvent, at concentrations of  $x$ ,  $\frac{x}{2}$  and  $\frac{x}{4}$  per cent.;  $x$  being in the neighbourhood of 1, and the two latter concentrations being obtained from the former by dilution. In order to express the viscosity, a tangent was drawn to the curve at a concentration of 1 per cent. Fol objected that the construction of a tangent involved a large personal equation,<sup>3</sup> and chose for the purpose of indicating the viscosity the area limited by the curve, the co-ordinate axes and the ordinate at a concentration of 1 per cent. He terms this quantity the “viscosity number.” Van Rossem<sup>4</sup> observed, from the examination of more than 500 viscosity-concentration curves, that the curves did not intersect, and, by

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Rubber*, London, 1911, p. 161.

<sup>3</sup> The experience of the present writer in regard to his own determinations of the viscosity of rubber solutions supports Fol's objection. The objection appears to have been sustained in subsequent controversy (Schidrowitz and Goldsbrough, *Koll. Zeit.*, X, 1913, 13, 46; Eaton, *I.R.J.*, 1913, 46, 315; Fol, *Meded. Delft*, 1916, p. 325; *Delft Communics.*, p. 78).

<sup>4</sup> *Loc. cit.*

treating a large collection of curves statistically, developed a simplification of the method of determining the "viscosity number," according to which it is sufficient to determine the viscosity at a single, arbitrary concentration. The "viscosity number" has been employed by the Delft Institute for expressing viscosity. Gorter proposed to express the viscosity by the logarithm of the relative viscosity of a 1 per cent. solution, which he terms the "viscosity index." And this method of indicating the viscosity has been employed by de Vries.<sup>1</sup> †

#### RELATION OF VISCOSITY TO VULCANIZING PROPERTIES

Van Rossem has calculated the degrees of correlation between, on the one hand, the "viscosity number" and, on the other hand, the coefficient of vulcanization and the breaking stress observed on subjecting a collection of plantation rubber samples (estate samples) to the fixed vulcanizing conditions of 1.5 hours at 148° in a 92.5/7.5 rubber-sulphur mix. For a collection of 113 samples of latex crêpe, the coefficient of correlation between the viscosity number and the vulcanization coefficient was  $+0.536 \pm 0.045$ ; for a collection of the same samples, together with 67 samples of sheet,  $+0.630 \pm 0.030$ ; for a collection of the former samples together with 95 diverse samples,  $+0.517 \pm 0.030$ . For 101 samples of latex crêpe, the coefficient of correlation between the viscosity and the breaking stress was  $+0.609 \pm 0.042$ . It should be noted that in the circumstances mentioned, viz. fixed vulcanizing conditions, the magnitude of the vulcanization coefficient and of the breaking stress is chiefly indicative of the rate of cure; and, therefore, that it may be concluded that in the collections of samples in question the coefficient of correlation between the viscosity and the rate of cure was in the neighbourhood of  $+0.5$ .

De Vries<sup>2</sup> has reviewed the data for a large number of samples<sup>3</sup>

<sup>1</sup> In order that a single measurement at any concentration in the neighbourhood of 1 per cent. may suffice, Gorter supposes that the log viscosity-concentration curves between concentrations of 0.5 and 1 per cent. are straight lines and, when produced, meet at a point 0.3 relative viscosity units for the zero point. Van Rossem concludes that this supposition is not in exact accord with the facts, and that "the viscosity index does not possess any single advantage over the viscosity number."

<sup>2</sup> *Loc. cit.*

<sup>3</sup> It is mentioned elsewhere ("Summary of Reports for 1916 and 1917 issued by the Board of the Association 'Central Rubberstation,'" *Batavia*, 1918, p. 16) that 2700 viscosity determinations were made in the investigation of the usefulness of viscosity measurements as a simple means of testing rubber and their relation to other properties.

† For a method of determining and expressing relative viscosity, recently agreed upon by a number of workers interested in the subject, vide *Archief*, 1920, 4, 122.

examined during the course of his researches, with the object considering the relations between viscosity and vulcanization properties. His general conclusion is that "as a rule a viscosity determination does not allow a definite conclusion as to the properties after vulcanization, unless it is certain that only one definite

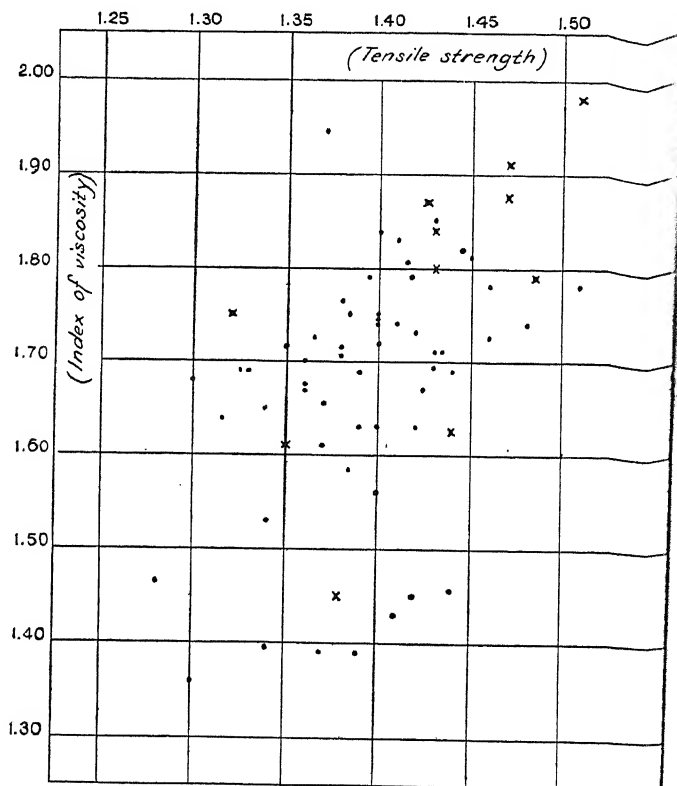


FIG. 38.—Viscosity and tensile strength of a number of estate samples (x smoked sheet, • latex crêpe).

and known factor has been at work. On the other hand, determined at the same time as other properties, the viscosity affords very useful aid in rubber testing, as it gives an insight into the group of factors which may have caused a deviation in the intrinsic quantities, and so allow one to give advice in a definite direction.

The vulcanization testing of the samples surveyed by de Vries was conducted in a 92.5/7.5 rubber-sulphur mix cured at 148

on the basis of a standard optimum curve; the "slope," the time required for the optimum cure (the "time of cure"), the breaking stress and breaking length at the optimum cure being determined. Hence the results allow of the relation of viscosity to the different aspects of vulcanizing quality being distinguished in a way that van Rossem's do not.

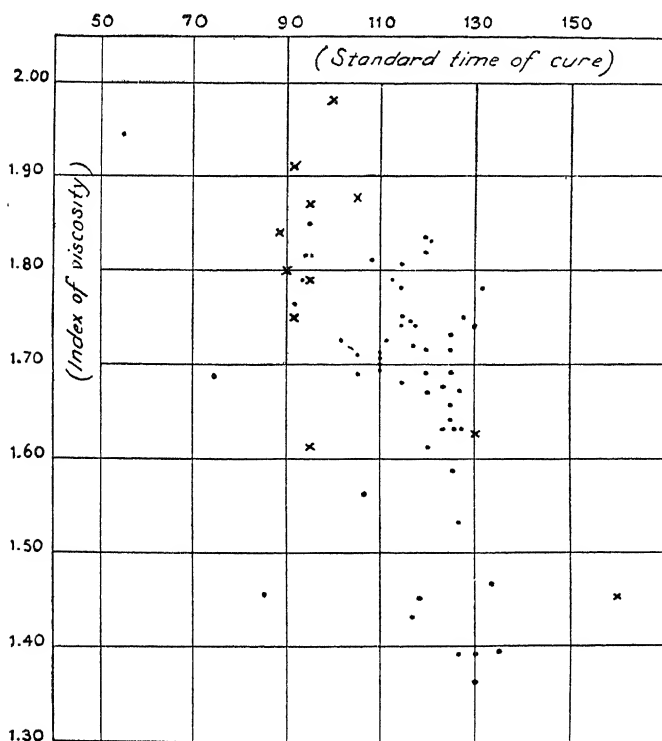


FIG. 39.—Viscosity and time of cure of a number of estate samples (x smoked sheet, • latex crêpe).

In the subjoined figures is shown the relationship between viscosity and tensile strength at the optimum cure and between viscosity and rate of cure for a collection of samples. The collection in question consisted of about 370 samples, all, with 4 exceptions, prepared on estates. The samples fall into 65 groups, each of which consisted either of a large sample which had been tested repeatedly, or of a mixture of samples, or of a number of samples



prepared on the same estate on different days or in different months. In the latter case, the mean of the results was taken. This arrangement of the data in groups was followed in order to eliminate experimental error as far as possible.

It is clear from these figures that in a random collection of samples of plantation rubber there is not any relation between, on the one hand, viscosity and, on the other hand, either tensile strength or the rate of cure sufficiently close to be of practical use.

*Factors in raw rubber preparation which influence the viscosity.* From an examination of the relation between viscosity and vulcanizing properties in relation to the different factors which may be involved in the preparation of raw rubber, de Vries concludes that the following relations can be detected:—

1. Few factors appear to affect both the viscosity and the tensile strength: as a general rule, even when the viscosity is affected the tensile strength is unaffected. The following, however, cause a decrease in both viscosity and tensile strength: (a) Heating at temperatures above 85°, or, in some cases, when prolonged above 70°. (b) Copper salts and alum. (c) The growth of chromogenic organisms in moist crêpe, producing orange to violet patches, reduces viscosity, tensile strength, rate of cure and slope. Deterioration of earth rubber is ascribed to a similar cause. (d) Rubber from young trees in the first period of tapping often shows a low tensile strength, with a low viscosity and a high rate of cure. The causal factor here has not been elucidated.

2. Many factors affect viscosity and rate of cure simultaneously in a similar direction. The following general conclusions—open to exceptions—were formulated: A. Chemicals, which are widely used in the preparation of rubber or which have been used occasionally, and which, at least in certain proportions, affect both viscosity and rate of cure are as follows:—(a) Producing an increase: sodium sulphite †, <sup>2</sup> sodium bisulphite †, <sup>2</sup> sodium carbonate, <sup>2</sup> sodium acetate. (b) Producing a decrease: formaldehyde, sodium thiosulphate, acetic acid, sulphuric acid, alum, formic acid. B. All conditions which favour maturation of the latex coagulum † increase and all which inhibit or retard maturation decrease the viscosity and the rate of cure. C. Anaerobic nature

† The factors indicated are also noted as producing an improvement in "slope." There is not sufficient evidence to decide whether a relationship exists in some cases between viscosity and slope.

<sup>2</sup> Observations by Ultée (*Archief*, 1918, 2, 331) agree with the above classification of the influence of these substances on viscosity.

coagulation increases both viscosity and rate of cure.<sup>1</sup> Treatment of the coagulum with warm water diminishes both viscosity and rate of cure.

Possibly many of the cases mentioned above could be summarized from one point of view by stating, generally, that basic substances tend to increase and acidic substances to decrease both viscosity and rate of cure. Spence and Kratz<sup>2</sup> have earlier pointed out that mere traces of acid bring about a very large reduction and of alkali a very large increase in the viscosity of rubber solutions.

3. In a number of conditions the viscosity and the rate of cure are not, as in the conditions grouped under 2, affected in the same, but in opposite directions. Among cases of such conditions are the following: (a) Coagulation by heat. (The rubber cures rapidly, but has a low viscosity.) (b) Age of trees. (Rubber derived from old trees often shows a high viscosity and a low rate of cure.) (c) A new tapping cut. (On opening a cut, the rate of cure is high and the viscosity low.) (d) Heavy tapping. (The effect is the same as with a new tapping cut.) The above and other cases suggest that there are physiological factors affecting the latex in the tree which may influence the viscosity and rate of cure in opposite directions.

De Vries concludes, by way of summary; that three groups of factors, which do not, however, embrace all the factors noted above, can be recognized as affecting the viscosity; namely: I. "Factors changing the state of aggregation or 'gelatination' of the rubber or the larger grouping that is destroyed and rebuilt during vulcanization. Viscosity is in this case affected, but the properties after vulcanization are not. The very drastic treatment to which the rubber is subjected during vulcanization equalizes, as it were, all superficial changes in the raw rubber falling in this group." II. Chemicals, which include some of those commonly used, as anti-coagulants, anti-oxidants, coagulants, disinfectants, and which affect parallel changes in the viscosity and the rate of cure, but do not affect the tensile strength. III. "Factors causing decomposition or oxidation of the rubber molecule. Viscosity and tensile strength are affected."

<sup>1</sup> Cf. Ultée (*loc. cit.*). Ultée finds anaerobic natural coagulation in the presence of sugar to lead to a reduction of viscosity, unless the sugar is previously fermented in latex serum. De Vries (*Archief*, 1917, **1**, 14) did not find coagulation in the presence of sugar to lead to a reduced viscosity.

<sup>2</sup> *Koll. Zeit.*, 1914, **14**, 265. Cf. Kirchhof, *Ibid.*, 1914, **15**, 33.

## CHAPTER XVIII

### CYCLES OF EXTENSION AND RETRACTION—HYSTERESIS

In the present chapter the rubber stress-strain curve will be regarded in an aspect somewhat different from that examined in Chap. X; the effect on the curve of repetition being considered, and the curve of retraction being considered as well as the curve of extension.

When an elastic material is subjected to deformation and then released, it does not re-trace during recovery exactly the same course that it traced during deformation; and, when the deforming force has been lifted, it is found that the material has not entirely regained, at all events immediately, its original form; that is to say, the course traced during recovery from deformation shows a lag or hysteresis, and the material is found to exhibit a set.

The occurrence of hysteresis in rubber was first remarked by Boileau,<sup>1</sup> in connection with the experiments on compression mentioned earlier (p. 249). Its more general aspects were first made the subject of close study by Bouasse and Carrière.<sup>2</sup> The study of cycles of extension and retraction as a means of rendering a judgment on the quality of samples of rubber has been employed by Schwartz, Beadle and Stevens, and others.

Hysteresis in rubber was first viewed in relation to the thermal behaviour of rubber during a cycle of extension and retraction by Villari.<sup>3</sup> As stated in Chap. XX, the heating effect on extension is greater than the cooling effect on retraction.

Villari noted in 1869 that if the extension of a sample of rubber was repeated, the stress-strain curve for the second extension lay somewhat higher than and approximately parallel to that for the first extension.

<sup>1</sup> *C. R.*, 1856, **42**, 933.

<sup>2</sup> *Annales de la Faculté des Sciences de Toulouse*, 1903, **5** (2), 257.

<sup>3</sup> *Cimento*, 1869, **2** (2), 301; *Rendic. Lomb.*, 1869, **2** (2), 767; *Ann. der Phys.*, 1872, **144**, 274. Cf. also Fessenden's conclusion—"the hysteresis is caused by the fact that, while the strip of rubber is being stretched, it gives out heat, and, whilst contracting, absorbs it again" (*J. Franklin Inst.*, 1896, **142**, 209).

## THE WORK OF BOUASSE AND CARRIÈRE

The observations of Bouasse and Carrière were all conducted on portions of the same material—a pure gum-sulphur compound, specific gravity 0.985, in the form of cords of 4 mm. diameter. The load was applied in a continuous fashion by feeding a copper chain into a container attached to the lower end of the rubber specimen. The rate at which the chain was fed in was regulated by means of a simple auxiliary arrangement. Each metre of the chain weighed almost exactly 50 g., and was marked off by a red thread on the chain. Between the container and the lower end of the (vertically arranged) rubber specimen a light scale was interposed. A telescope was placed so as to view the scale and the passage of the chain at the same time. In this way simultaneous readings of the extension and the load could be made at load intervals of 50 g.

Some of the results of this investigation are given below.  $L_0$  = the initial length of the specimen under the constant load to which it was subject at all times owing to the weight (61 g.) of the attachments (grips, etc.).  $L$  = the length at any time.  $L/L_0 = \Lambda$ , *i. e.* the percentage increase in length divided by 100.  $\pi$  represents 1 m. of chain (approx. 50 g.). The unit of length is 0.1 mm. Unless otherwise stated, the rate of loading was 1 m. of chain per 27 seconds.  $T_0$  and  $T$  indicate the time under the loads at the lower and upper points of the cycle respectively.

The existence of lag in the recovery may be seen by a glance at the figures in the following table, which represent the increments of extension and of retraction corresponding to each load interval of  $2\pi$  during a cycle in which the load was increased from 0 to  $30\pi$  and then decreased from  $30\pi$  to 0.

TABLE CXXVI

$L_0 = 1470$ . Load intervals:  $2\pi$ .

Extension	.	.	173	257	382	558	694	736	733	673
Retraction ( <i>Contd.</i> )	.	.	94	83	78	99	124	162	228	370
Extension ( <i>Contd.</i> )	.	.	624	582	535	507	447	377	319	
Retraction	.	.	734	1156	1644	1182	718	472	342	

The curves corresponding to this cycle are shown on the left of Fig. 40.

*Repetition of cycle.*—In the above cycle, the extension was from  $\Lambda_0 = 1$  to  $\Lambda = 6.16$ , and the retraction from  $\Lambda = 6.16$  to  $\Lambda_0 = 1.20$ . The cycle between the same load limits was repeated,

without halts, seven times. The extreme points of the successive cycles were as follows :—

TABLE CXXVII

$\Lambda_1$	.	.	6.16	6.68	6.90	7.04	7.17	7.27	7.36	7.43
Differences	.	.	52	22	14	13	10	9	7	
$\Lambda_0$	.	.	1.20	1.23	1.25	1.28	1.28	1.28	1.28	1.28

It will be observed that, as the number of cycles to which a sample of rubber is extended is increased, the course of the cycle tends to become *fixed*. Further, the difference between the

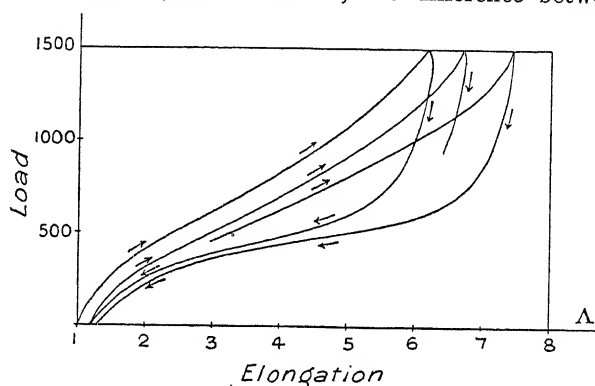


FIG. 40.

first and the second cycles is much more marked than the difference between any other two succeeding cycles. In Fig. 40 are shown the curves for the first, a part of the second and a part of the eighth cycle.

As the number of cycles increases, (a) the inclination at the outset of the cycle becomes greater; (b) the tangent of inflexion on the extension curve becomes steeper; (c) the inclination at the end of the extension curve becomes smaller, *i. e.* the rubber becomes less deformable for the final increment of load; (d) the tangent of inflexion on the retraction curve becomes steeper; (e) the inclination of the conclusion of the cycle varies only a little. As regards the inclination at the outset of the retraction curve: this is considered as depending upon two opposed effects, namely, a tendency of the rubber to lengthen owing to after-effect (cf. Chap. XIX) and a tendency of the rubber to shorten owing to the actual diminution of the load. In the immediate neighbourhood of the extremity of the cycle, the former tendency always prevails. In the case quoted, there

was in the first and second cycles a clear elongation on the "retraction" curve over the first load interval,  $-\pi$ ; in the third cycle there was no change in length over this interval; beyond the sixth cycle there was a distinct shortening.

Schwartz<sup>1</sup> concluded that the area of the loop became fixed more quickly with a higher grade than with a lower grade rubber. For a high-grade rubber, containing 88 per cent. of Para, which he examined, the area of the loop for successive cycles became constant after about the sixth cycle.

The same author found the relation of the increase of length at the extreme point of succeeding cycles traced at constant speed to be related in the following way: If the increments of extension at the extreme point of each cycle are plotted against the logarithms of the number of the cycles (*i. e.* log. time, since the time for describing each cycle is constant), a straight line is obtained. The extension for the successive cycles from the second onwards follows the law—

$$\text{Extension} = a + b \log. \text{ no. of cycle,}$$

where  $a$  represents the extension due to the second cycle, and  $b$  the increment of extension due to subsequent cycles. Beadle and Stevens<sup>2</sup> state that their experience confirms the existence of a linear relation between the extension for each successive cycle and the log. of the number of the cycle.

*Cycles of different lengths.*—The shorter the cycle, the narrower is the hysteresis loop, *i. e.* the more nearly does the retraction curve coincide with the extension curve. This is seen in the following observations: A new specimen of the rubber cord under investigation was subjected successively to cycles of ascending and descending magnitude of which the upper limits were 250, 500, 750, 100, 750, 500, 250 g. (Cycles 1-7); the lower limit in each case being 0 g. Each cycle was repeated until it was "fixed," before proceeding to the next one. The maximal differences of the abscissæ corresponding to an equal load were as follows:—

TABLE CXXVIII

Cycles of (g.)	250	500	750	1000
Ascending . . .	61	167	286	533
Descending . . .	61	148	236	—

<sup>1</sup> *J. Inst. Elec. Eng.*, 1910, 44, 693.    <sup>2</sup> *Rubber Industry*, 1911, p. 267.

Results obtained in this experiment may also serve to illustrate a general rule which Bouasse and Carrière found to hold in experiments under a large variety of different conditions, namely: "A variation of the load always facilitates change of length." Thus, for example, they "find that in a given time the rubber can be extended less under a constant load  $x$  than under a load variable between 0 and  $x$ ."<sup>1</sup> Comparing Cycles 1-7 among themselves, so as to note the difference between ascending and descending cycles between the same load limits, we find—

TABLE CXXIX

	Amplitude of cycles of (g.)			
	250	500	750	1000
Ascending . . .	789	2623	4739	6711
Descending . . .	1055	3176	5238	—
Differences . . .	334	447	501	—

The effect of the previous operations on a cycle when the cycle comes to be repeated is very considerable. It is proportionately greater for the Cycle 250 g. than for the Cycle 750 g. In the following figure are shown Cycle 4 in full and the extremities of the other cycles.

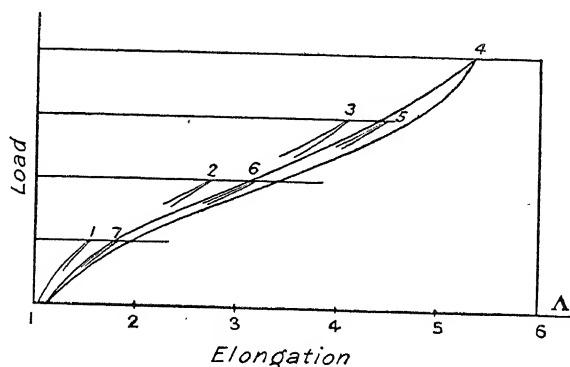


FIG. 41.

A further general conclusion which Bouasse and Carrière formulate is as follows: "Between two given loads, there exist

<sup>1</sup> Note in this connection the greater extension observed in the Bureau of Standards' tests (p. 279) when comparing repeated stretching with a single stretch.

an infinite number of fixed cycles which depend on the prior operations; and this is so even when, during the operations which separate two fixations, the rubber is subjected to greater loads than those to which it was subjected during the first fixation." The authors give a number of interesting experiments illustrative of this conclusion, showing, for example, how greatly the course of a cycle between given loads may be influenced by the execution of sub-cycles within the limits of the main cycle.

*Influence of rate of loading and unloading.*—(a) Other things being equal, a cycle traced at a higher rate has a smaller amplitude and a greater area or thickness than a cycle traced at a

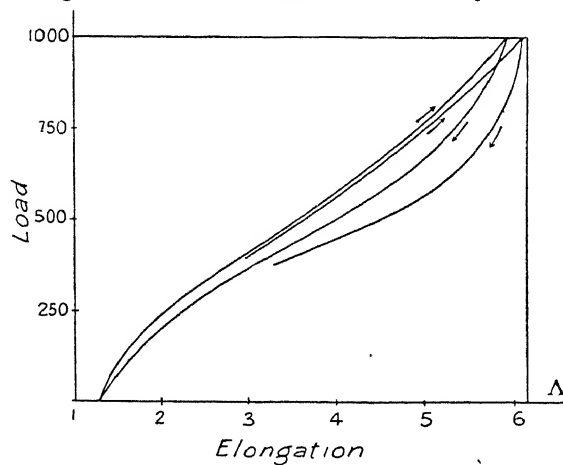


FIG. 42.

lower rate. A specimen was subjected to cycles of 0–1000 g. at different rates,  $V = 100$  g. in 9 sec.,  $v = 100$  g. in 136 sec.  $T_0 = T_1 = 0$ . The amplitudes of successive cycles, measured on the extension curve, were as follows:—

TABLE CXXX

V	.	.	.	7980	8080	8175	8250	8290
v	.	.	.	8679	8791			
V	.	.	.	8709	8630	8660	8660	
v	.	.	.	9031	9067			
V	.	.	.	8935				

Fig. 42 shows on the right a cycle traced at speed  $V$ , and on the left a cycle traced at speed  $v$ . The difference in area of the loops which is observable is due chiefly to difference in the retraction curves.



Schwartz<sup>1</sup> also found the area of the loop to be larger at a higher speed than at a lower one. His ratio of speeds was only 1:5, and the difference in areas only small.

(b) A cycle traced between two points with a high rate of load may have practically the same amplitude as a cycle traced between the same points with a low rate of loading, if suitable arrests are made in the loading. In the following experiment the rates of loading were  $V = 100$  g. per 4.7 sec.,  $v = 100$  g. per 184 sec. Cycles 0-1000 g. were traced. Rate  $V$  would require for tracing a complete cycle 94 sec., and rate  $v$  61 min. 20 sec. The cycles at  $V$  were traced, with eight periods of rest, so that the total time occupied in tracing the cycle was the same at the high rate of loading as at the low rate. Thus the rests were about 7.5 min. in length. They were arranged to occur at point such that  $P dt$  was the same. The rests occurred at 125, 375, 625 and 875 g. The length of the rubber specimen at these loads is shown in the following table. In the case of the higher rate of loading, the length at the beginning and the length at the end of the rests is given.

TABLE CXXXI

Length at load of (g.)		125	375	625	875
Extension $\left\{ \begin{matrix} v \\ V \end{matrix} \right.$	$\cdot$	579	2467	4822	6762
		530-569	2352-2529	4730-4849	6659-6851
Retraction * $\left\{ \begin{matrix} v \\ V \end{matrix} \right.$	$\cdot$	692	2653	5309	7104
		661-792	2602-2720	5230-5300	7033-7000

\* Read right to left.

Having regard to the degree of exactness which may be expected in such an experiment, it may be stated that in the case of the cycle at  $V$ , the horizontal course of the curve during each rest brings the curve approximately on to the continuous curve of the cycle at  $v$ .<sup>2</sup> This experiment, the authors remark, "has a considerable theoretical significance. There is always a temptation to exaggerate the importance of disturbances, of small irregularities in the rate of loading, etc. A more systematic irregularity than the preceding one could not be imagined; yet the experiment shows that its total effect is almost negligible:

<sup>1</sup> *Loc. cit.*

<sup>2</sup> The phenomena observed, Bouasse remarks, are quite analogous to those which he found for the curves of torsion of metallic wires.

the cycles retain, on the whole, the form and the same amplitude."

*Influence of temperature.*—A cycle traced at a higher temperature has a smaller area than one traced at a lower temperature. The following shows the difference of the abscissæ corresponding to the same load for cycles of 1150 g. traced successively at 12°, 60° and 12° ( $L_0 = 1520$ ): 12° . . . 1981, 2335; 60° . . . 295, 209; 12° . . . 2400, 2418. The following figure shows a cycle at 60° (left) and one at 12° (right).

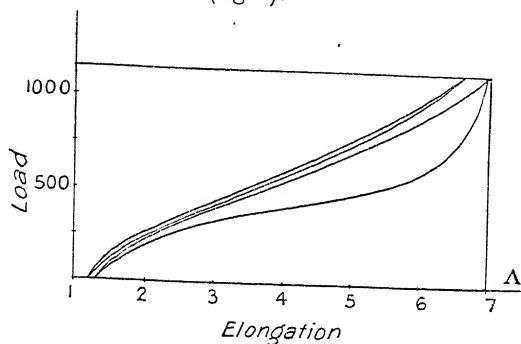


FIG. 43.

The influence of a change of temperature on the amplitude of the cycle is determined largely by the whole course of the operations in question. A number of experiments under rather complicated conditions were made.<sup>1</sup> Under some conditions increase of temperature led to a greater amplitude, and under some other conditions to a smaller one.

Shedd and Ingersol<sup>2</sup> have made observations on the form of the hysteresis loop, or, as they call it, the viscosity loop, at a number of different temperatures. Their results confirm the conclusion that increase of temperature reduces the area of the loop. The temperatures employed ranged from 11° to 93°. Beyond 60° the effect of increase of temperature was only slight.

#### THE SCHWARTZ MACHINE

A valuable contribution to the study of cycles of extension and retraction with rubber has been made by Schwartz in the shape of a machine which gives an autographic record of the

<sup>1</sup> *Loc. cit.*, pp. 279–82.

<sup>2</sup> *Phys. Rev.*, 1904, **19**, 107. This investigation of hysteresis in rubber calls only for brief mention. The data given in the paper are incomplete.

stress-strain curves. In his own experiments with the machine, Schwartz used a strip test-piece, but the machine can readily be adjusted to use rings. The load is applied through springs—of different strengths, according to the class of rubber under test. The autographic record is made on a movable table attached to the test piece and to the springs by means of cords and pulleys.

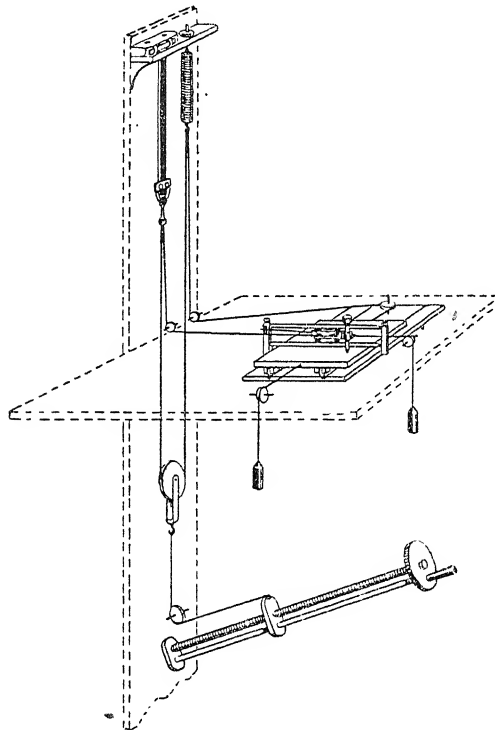


FIG. 44.—The Schwartz hysteresis machine.<sup>1</sup>

The movement of the table is directed by the load, and that of the pencil by the extension of the rubber. Both the pencil and the table are attached by cords to counterweights; the load thus being divided between the test piece and the spring.

The machine was designed in the first place for the mechanical examination of rubber for the insulation of electric cables. Its limitation from the point of view of its more general use, and particularly of its use in the testing of the high-grade com-

From the *Journal of the Institute of Electrical Engineers*.

pounds in which research work on the vulcanization of plantation rubber has generally been conducted, lies in its light construction and the comparatively small elongations for which it is suited; the maximum extension used being generally 400 per cent.

A heavier machine, which would be capable of giving autographic records both of cycles of great amplitude and of extensions to the breaking-point, would undoubtedly be of great value. The Schwartz machine would, however, require very considerable modification to make it capable of this.

#### CYCLES AND THE EVALUATION OF RUBBER

The employment of the Schwartz machine for discriminating between samples of different quality or at different states of cure has been investigated to some extent by Schwartz, Beadle and Stevens and van Rossem. The following table shows the results obtained by Schwartz for a number of samples examined on the hysteresis machine, with a load sufficient to produce an extension of 100 per cent. in the first cycle. It shows also the results obtained by Stevens for the breaking figures and set of the same samples.<sup>1</sup>

TABLE CXXXII

Reference no.	Composition of mix—rubber, factice, ZnO, sulphur.	Cured for 3 hrs. at	Area of first loop (ins. <sup>2</sup> )†	Max. extension (in.) in successive cycles.	P <sub>B</sub>	L <sub>B</sub>	Percentage recovery. Stretched to L=400.	
							After ½ hr.	After 6 hrs.
1379	60 0 37 3	127.5°	0.46	3.00 3.38 3.53 3.64	0.314	978	88.9	92.7
1381	50 10 37 3	127.5°	0.53	3.00 3.48 3.72 3.85	0.287	1000	84.1	91.9
1382	50 10 37 3	132.0°	0.74	3.00 3.62 3.95 4.16	0.362	964	87.2	93.6
1389	40 20 37 3	132.0°	0.95	3.00 3.74 4.13 4.46	0.282	950	85.0	93.5
1390	40 20 37 3	135.5°	1.42	3.00 3.83 4.35 4.75	0.358	950	79.3	89.4
1391	30 30 37 3	135.5°	2.37	3.00 4.26 5.22 —	0.271	858	63.9	81.6
1392	30 30 37 3	139.0°	3.37	3.00 4.35 5.36 —	0.238	670	Broke	Broke

† This represents the work expended in the rubber. Schwartz attaches particular importance to this quantity.

In hysteresis tests on rubber a definite load limit would appear to recommend itself in preference to a definite extension limit. Beadle and Stevens<sup>1</sup> have used cycles traced with a constant load limit of 0.200 kg./mm.<sup>2</sup> for the examination of rubber samples. The test pieces consisted of strips 50 mm. in length between the grips, 5 mm. wide and 1 mm. thick. Five cycles are traced with each sample. The following terms are employed in expressing

<sup>1</sup> *Rubber Industry*, 1911, p. 265.

the results of the tests: *Cyclic fatigue* expresses the loss to support a given load and the consequent progressive increase in length produced by successive applications of the same load. It is given by (length at fifth cycle—length at first cycle) ÷ length at first cycle. *Cyclic remainder* represents the percentage difference between the length of the sample at the conclusion of the fifth cycle and the original length. It is given by the distance between the retraction curve at the conclusion of the fifth cycle and the original length.

The following table allows of a comparison being made of samples of data obtained from the cyclic diagrams with the breaking figures (determined with stationary rings) and the set determined by stretching to  $\Lambda = 4$  for twenty-four hours and allowing six hours' recovery.

TABLE CXXXIII

No. of sample.	Elongation.		Cyclic remainder.	Cyclic fatigue.	P <sub>B</sub>	L <sub>B</sub>	P <sub>B</sub> × L <sub>B</sub> /100
	1st cycle.	5th cycle.					
1	292.0	459.6	29.2	23.9	0.524	990	5.19
2	302.0	464.8	30.0	23.2	0.580	990	5.73
3	306.8	480.8	37.6	24.8	0.445	920	4.09
4	356.8	554.0	45.2	28.2	0.432	1010	4.37
5	376.4	603.6	48.8	32.4	0.410	950	3.90
6	416.4	659.2	60.0	34.7	0.337	1040	3.52
7	424.4	669.6	65.2	35.0	0.315	920	2.90
8	421.4	686.8	64.0	37.9	0.355	980	3.48
9	432.0	688.0	75.2	36.6	0.290	920	2.65
10	416.8	657.6	79.2	34.4	0.218	940	2.99

From an examination of the data in the above table, it appears that, broadly speaking, the judgments rendered by the samples by the cyclic test are similar to those rendered by the breaking-point.

The Delft Institute<sup>1</sup> examined 128 samples of plantation rubber—100 samples of crêpe and twenty-eight samples of sheet, all cured under the same conditions (cf. p. 362), on the Schenck machine, with reference to the load necessary to produce an elongation of 400 per cent. Van Rossem,<sup>2</sup> treating the results of the examination statistically, found the coefficient of relation between this load and the vulcanization coefficient to be  $+0.851 \pm 0.016$ . For a similar collection of 346

<sup>1</sup> *Delft Communics.*, pp. 165–8.

<sup>2</sup> *Loc. cit.*, pp. 113, 151.

(237 crêpes and 109 sheets), he found the coefficient of correlation between the load necessary to produce an elongation of 850 per cent., as read from the stress-strain curve given by the Schopper machine, and the coefficient of vulcanization to be almost the same as this figure, viz.  $+0.867 \pm 0.009$ . A comparison was made of the most probable curve corresponding to various vulcanization coefficients (range 1.5 — 6.0), as secured on the Schwartz machine with an elongation of 400 per cent., and as secured on the Schopper machine with elongation to break. It was found that the curves obtained on the two machines corresponded. It was concluded that the diagram on the Schwartz machine for a given rubber sample could be deduced from the diagram for it on the Schopper machine, and, vice versa, that the diagram on the Schopper machine could, at all events as regards its early part, be deduced from the diagram on the Schwartz machine.

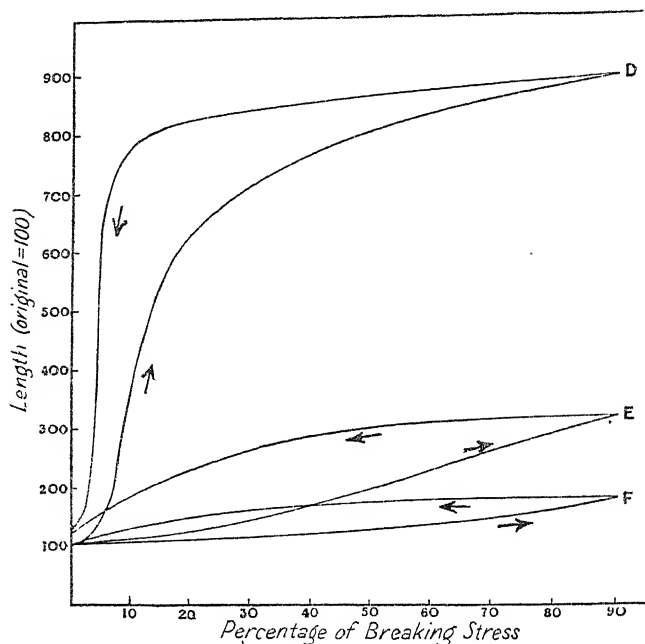
It may be concluded that for rubber samples of the same class—in the present case, latex plantation rubbers—there is an approximate correspondence between the length at 400 per cent. and at 850 per cent. elongation. This is what would be expected from knowledge of the fact that for a number of rubber samples in such a class the stress-strain curves taken to the breaking-point seldom intersect but are similar in form.<sup>1</sup> But, while it may be agreed that tests on the Schwartz machine when confined to describing a single cycle to 400 per cent. “do not disclose any new points of view,” it would seem too sweeping to conclude, on the data produced, as the Delft Institute does, that “testing with the Schopper machine makes the use of the other machine superfluous.” A chief object of the Schwartz machine is to study the effect, not merely of a single extension, but of a repetition of cycles of extension and retraction. And the work of Bouasse and Carrière suggests that a cycle for one rubber should be “fixed” for the purpose of comparison with another rubber. The Delft investigation would appear to be insufficiently wide to warrant the sweeping final conclusion mentioned above.

The examination of samples of rubber by means of cyclic tests, involving the repetition of extensions short of the breaking-point, have, as Beadle and Stevens<sup>2</sup> point out, the following advantage

<sup>1</sup> Cf., however, remarks on p. 352 concerning the significance of differences in “slope” in regard to the relation of intermediate extensions in comparing the tensile properties of rubber samples.

<sup>2</sup> *Rubber Industry*, 1911, p. 274.

over tests in which merely the breaking figures are obtained, namely, that "they can be made with very great accuracy, the error on a repeat test does not usually exceed 1 per cent., while tensile strength tests vary from 5 to 20 per cent. when repeated; indeed, at least ten separate tests must be made and the mean taken to arrive at an approximately correct figure." (Cf. the

FIG. 45.<sup>1</sup>

Rubber D is a high-grade material ( $P_B = 0.752$ ,  $L_B = 910$ ). E is a low-class red sheet (Ash = 41.5 per cent.,  $P_B = 0.120$ ,  $L_B = 368$ ). F is a low-class, rather hard, grey rubber sheet (Ash = 57.5,  $P_B = 0.135$ ,  $L_B = 195$ ).

discussion on the fortuity affecting breaking figures, pp. 343 *et seq.*)

It is probably safe to say that the use of hysteresis tests in the study of the tensile properties of rubber samples has not yet seen its full development. To mention only one possibility: future investigation may, not impossibly, find that they are of value in the study of the inter-relation of thermal and mechanical

<sup>1</sup> From *Rubber*, by P. Schidrowitz (Methuen, 1911). By permission of the author and publishers.

effects in rubber compounds of different composition (cf. Chap. XX). One of the chief limitations of the Schwartz machine is the comparative lowness of the extensions for which it is suited. A machine for cyclic tests capable of taking the specimen to great extensions, so as to trace sufficient of the flat portion of the extension curve to allow of readings of "slope," would probably be of considerable value, particularly if it also permitted of extensions to the breaking-point.

*Loops for low-grade rubber compounds.*—The samples of rubber dealt with in this chapter have been mostly high-grade samples—pure gum-sulphur compounds. The curves in Fig. 45, given by Schidrowitz,<sup>1</sup> will indicate the widely different character which the hysteresis loops may exhibit in the case of low-grade rubber compounds from that exhibited in the case of highly extensible rubber.

<sup>1</sup> *Rubber*, 1911, p. 232.



## CHAPTER XIX

### ELASTIC AFTER-EFFECT

UNDER the somewhat clumsy designation "elastic after-effect"<sup>1</sup> are included particularly the creep with which a further elongation follows on the initial lengthening if a load is left to act for some time on a strip of rubber, and the creep with which, following on the initial retraction due to the removal of a load, a strip of rubber approaches its original length. Elastic after-effect is clearly of importance in regard to the technical application of rubber. In rubber testing it is not infrequently taken into account by determining the "set" present under certain conditions; but, as the following discussion will suggest, its further study in connection with the testing of rubber would probably be advantageous.

The absolute magnitude of the after-effects which may be shown by rubber is much greater than that of the after-effects which most other elastic materials show. Dietzel<sup>2</sup> appears to have been the first (in 1857) to record observations on after-strain in rubber. He distinguishes clearly between fore-strain, after-strain and set. He stretched a rubber rod of  $\frac{1}{8}$  in. square cross section with loads increasing from 1-29 gms.,<sup>3</sup> and, in addition to the fore-strain, made observations on the after-strain produced during twenty-four hours. He concluded that, roughly speaking, the elastic after-strains were proportional to the loads. The after-strain developed during twenty-four hours fell from one-quarter to about one-twelfth of the fore-strain, as the load increased from 1 to 29 gms.

### TORSIONAL AFTER-EFFECT

*Neesen's observations.*—Neesen<sup>4</sup> investigated after-effect in rubber threads following subjection to torsion. Kohlrausch<sup>5</sup>

<sup>1</sup> *Ger.*: Nachwirkung. *Fr.*: Réactivité.

<sup>2</sup> *Polytechnisches Centralblatt*, 1857, 689-94. (*Fortschr. Phys.*, 1857, 143; Todhunter and Pearson's *History of the Theory of Elasticity*, Vol. II., Part I., 752.)

<sup>3</sup> The elongation produced by the highest load can have been only a few per cent. of the initial length.

<sup>4</sup> *Monatsber. K. Preuss. Akad. Wiss.*, 1874, 141 (preliminary discussion); *Ann. der Phys.*, 1874, 153, 498 (full account).

<sup>5</sup> *Ann. der Phys.*, 129, 337; 128, 1.

(cf. *infra*) had previously concluded that the after-effect in metallic wires which had been subjected to torsion was given by the expression—

$$\phi = Ce^{-at^m},$$

where  $\phi$  is the distance from the final position of rest at a time  $t$ , and where the other quantities are constants,  $m$  being  $< 1$ . Neesen, from his experiments on rubber threads, concluded that elastic after-effect in rubber proceeded according to simple exponential curves, and that the following expression, simpler than Kohlrausch's, was applicable; namely,

$$\phi = Ce^{-\beta t}.$$

The apparatus employed for this investigation appears to be well adapted to the study of torsional after-effect in rubber. Yet Neesen's investigations can only be regarded as merely preliminary. The threads were 250 mm. long and 1.3 mm. in diameter. The amount of torsion applied varied between  $15^\circ$  and  $70^\circ$ . By means of a mirror attached to the thread and a scale placed at a distance, observations of the creep of the thread back towards its original position were made. Several minutes were required after the thread had been released from torsion before its vibrations ceased; and observations on the elastic after-effect were not begun until ten minutes had elapsed. Most of the series of observations covered only the period between ten and twenty minutes. In some cases observations were made up to seventy minutes; and it was found that for this further period the expression given above did not fit the data. If, however, a second term,  $C_1 e^{\beta_1 t}$ , was added to the equation,<sup>1</sup> the agreement between calculated and observed values was also satisfactory for the later period.

A noteworthy feature of Neesen's observations is that they afford a good illustration of the fact, which Neesen overlooked, and which Kohlrausch failed to appreciate, but which Bouasse later emphasized, that each preceding operation on a sample of rubber has an influence on each subsequent operation; and it is noteworthy that Neesen found continually he could not reproduce in a subsequent experiment figures which he obtained in an earlier one; even though the conditions (angle of torsion, duration of torsion, temperature, etc.) were apparently identical:—although the effects observed proceeded according to the simple exponential expression, the constants in the expression were of different

<sup>1</sup> The equation refers back to theoretical considerations of O. E. Mayer, *Ann. der Phys.*, 1874, and in its complete form is  $\phi = \Sigma Ce^{-\beta t}$ .

magnitude. He endeavoured to ascertain the influence of variation in the angle of torsion, duration of torsion and temperature on the after-effect, but could recognize no regularity in the change of the constants with change in these factors. Undoubtedly this lack of regularity was due to the unrecognized influence of previous operations on subsequent ones.

Kohlrausch, a little later, in a discussion of after-effect in rubber, recognizes to a certain extent that a succession of operations is not without effect on the condition of the rubber, for he states:—

“The chief difficulty in observations on after-effect, namely, the determination of the final equilibrium form, showed itself, as was to be expected, very markedly in the case of rubber. It was more difficult than with metals to avoid over-stepping the elastic limit. The position of rest was subject to slow change, partly no doubt connected with fluctuations of temperature, but also with causes which I could not discover. Probably a change of the material with time, a rearrangement of the particles, is one of them.”<sup>1</sup> Elsewhere he states: “Remains of old after-effects come and appear as over-stepping the elastic limits. The matter demands and well deserves an exhaustive examination.”

Yet he fails to allow adequately for the influence of previous operations on subsequent ones. This influence must be considered as particularly important where the measurement of such comparatively small quantities as those concerned in after-effect is in question. Kohlrausch worked throughout on the same two samples of rubber, and was satisfied to assume that, if the interval between two successive experiments on the same sample was such that after one experiment “noticeable displacement no longer occurred over a period of fifty minutes” before a succeeding experiment was started, each operation was uninfluenced by the preceding ones. The more recent work of Bouasse and Carrière on elastic after-effect in rubber shows conclusively that such an assumption is unjustifiable.

*Kohlrausch's work.*—Kohlrausch<sup>2</sup> subjected Neesen's work to a damaging criticism. He pointed out, among other things, that Neesen made no observations over the first ten minutes; and, further, that the piece of the curve which he observed was so short and the number of constants in his expression so considerable that his work was not well suited to establish the law which the after-effect may follow. Kohlrausch then himself undertook

<sup>1</sup> *Ann. der Phys.*, 1876, **158**, 337.

<sup>2</sup> *Ibid.*, 1875, **155**, 579.

observations on the after-effect following the torsion of rubber threads, and concluded that its course is given by the same expression as that which he had found to apply to metallic wires. The following is an account of Kohlrausch's investigation:—

The velocity with which a deformed body approaches its position of rest by virtue of elastic after-effect is directly proportional to the distance,  $x$ , from that position at the time,  $t$ , and inversely proportional to a power of  $t$ .

$$-\frac{dx}{dt} = a \frac{x}{t^n}.$$

That is—

$$(1) \quad x = Ce^{-at^m}, \text{ where } m = (1 - n) \text{ and } a = \left(\frac{a}{1 - n}\right).$$

In the case where the deformation to which the material is subjected is small, we have the simple form  $-\frac{dx}{dt} = a \frac{x}{t}$  or

$$(2) \quad x = \frac{C}{t^a}, \text{ where } a = am.^1$$

The experimental arrangement was similar to that of Neesen, the deflection from the position of rest being read by means of a mirror and scale. The rubber used consisted of two specimens of square cross section; the side of the square being 0.9 mm., the weight of 1 mm. 0.98 mgs., and hence the specific gravity 1.2. The free length when fastened in the torsion apparatus was 178 mm. With the experimental arrangement employed, the vibrations were damped sufficiently to permit of observations of the elastic after-effect thirty seconds (Thread I) or forty seconds (Thread II) after the removal of the torsion. In the first series of experiments the duration of the period for which the rubber was subjected to torsion was only half a minute; and the after-effect was found to be expressed very closely by the simpler formula, (2). The following is a typical series of observations:—

TABLE CXXXIV

Temperature, 18.7°; angle of torsion, 82.5°;  $x$  is given in scale divisions (1 division = 0.0206°);  $\Delta$  denotes the difference between the observed and calculated values.

$t$ (min.)	0.66	1	1.5	2	3	5	7	10	15	20	30	50	1000
$x$	209.7	173.6	143.4	125.5	104.3	83.2	71.8	61.5	51.3	45.3	37.7	29.5	20.5
$\Delta$	-2.2	-0.7	+0.7	+1.1	+1.1	+0.6	+0.2	-0.1	-0.2	-0.4	-0.2	+0.3	+1.3

<sup>1</sup> In the choice of a position of rest in any given case, there is, confessedly, a certain element of arbitrariness. In the case of recovery from stretching, it is taken as the original length, but, in other cases, its determination is more arbitrary.

As regards the influence on the after-effect of the angle of torsion: Kohlrausch concluded that the constant  $C$  (the after-effect present at time,  $t = 1$  min.) was proportional to the angle of torsion,  $\phi$ , and could be represented as  $C = 0.0428$  degrees. The exponent  $a$ , which represents the velocity of disappearance of the after-effect, diminished with increase of  $\phi$ , and could be represented as,  $a = 0.67 - 0.003 \phi$ .

In the second series of experiments the duration of torsion was longer, and  $m$  assumed a definite value, so that it was necessary now to use formula (1), in order to express the course of the after-effect. The following gives some of the data. For the purposes of comparison, an experiment on the same thread with a short duration of torsion and a large angle of torsion is included (No. 2).

TABLE CXXXV

*Recovery from torsion of a rubber thread*

$x$  is in scale divisions (1 scale division =  $0.0245^\circ$ )

$t$ (min.).	No. 3. Temperature $16^\circ$ . Angle of torsion = $43^\circ$ . Duration of torsion 15 min.		No. 4. Temperature $14^\circ$ . Angle of torsion $43^\circ$ . Duration of torsion 75 min.		No. 2. Temperature $16^\circ$ . Angle of torsion $180^\circ$ . Duration of torsion 10 sec.	
	$x$ .	$\Delta$	$x$ .	$\Delta$	$x$ .	$\Delta$
0.5	175	+ 8	—	—	—	—
0.7	160	+ 6	240	— 2	101	— 6
1	144	+ 4	225	— 1	87	— 3
1.5	126.7	+ 1.4	207.1	+ 0.2	73.6	— 0.6
2	114.8	+ 0.3	194.0	+ 0.2	66.0	+ 0.2
2.5	105.7	— 0.3	185.0	+ 0.6	60.6	+ 0.8
3	—	—	170.2	— 0.2	54.0	+ 0.7
4	87.2	—	164.6	+ 0.6	51.8	+ 0.5
5	78.9	— 0.7	155.1	+ 0.4	48.0	+ 0.5
7	67.0	— 0.5	140.7	+ 0.4	43.3	0.0
10	55.5	— 0.1	125.8	— 0.2	38.5	— 0.2
15	44.2	+ 0.1	109.1	— 0.4	34.1	+ 0.3
20	37.1	+ 0.3	96.9	+ 0.1	31.1	— 0.8
25	32.5	0.0	87.7	+ 0.6	29.1	— 1.0
30	28.7	+ 0.2	80.9	+ 0.5	27.1	— 0.7
40	23	0.0	71.4	— 0.4	24.5	— 0.6
50	20.2	0.0	—	—	22.7	— 0.5
70	15.7	0.0	52.6	— 1.2	19.6	+ 0.2
73	—	—	45.9	— 0.5	—	—
90	14.0	— 0.4	—	—	16.9	+ 1.3
120	9.9	+ 0.1	—	—	14.3	+ 2.2
176	6.9	+ 0.2	—	—	—	—
276	—	—	18.4	+ 2.4	—	—

The influence of the duration of torsion on the velocity of recovery is illustrated by the above data. It will be observed

that the after-effect—the sub-permanent “set” at any moment—following fifteen minutes’ subjection to a torsion of  $43^\circ$  is considerably greater than that following ten seconds’ subjection to a torsion more than four times as large, viz.  $180^\circ$ . The constants in the expressions representing No. 3 and No. 4 respectively are :—

	C.	a.	m.
No. 3 . . .	787.8	1.675	0.20
No. 4 . . .	433.6	0.6607	0.273

Kohlrausch found, generally, that the exponent  $m$  increased with increasing duration of torsion.

#### TENSILE AFTER-EFFECT

*Kohlrausch's experiments.*—Kohlrausch also made experiments on after-effect as it relates to the extension of rubber, using the same kind of rubber as that employed for his torsional experiments. The specimen was fastened on a wall support, and the movement of a mark near its lower end followed by means of a telescope and scale. A small scale-pan was suspended from the thread, and from the pan was hung a small, vertical, hollow, brass cylinder, which dipped into a vessel of water, and had for its purpose the damping of any lateral vibrations in the thread. The constant load, due to the pan, etc., which the thread was under continually, was 4.1 grams. The length of the thread under this load was 2300 mm. Before the observations on after-effect were begun, the thread was extended by about 600 mm. for twenty minutes, and was then left to itself for a day.

*After-retraction.*—The first set of experiments deals with after-retraction, *i. e.*, recovery from stretching. Kohlrausch's method of stretching the thread was not very satisfactory. The end was grasped by the hand; the thread was extended by a length,  $l$ ; it was held at this length for a minute, and was then led back quickly but cautiously<sup>1</sup> to its unstrained position. Within ten seconds of its release, readings could be taken, but the first reading cannot claim to exactness. It was found that values of  $x$ , the distance of the thread at a time,  $t$ , from its position of rest (taken in the extension and retraction operations as the original length), could be expressed by the same formula as applied to recovery from torsion.

As an example of the results obtained, the following experiment may be quoted.  $\Delta$  is the difference between the observed values

<sup>1</sup> Rasch aber behutsam.

of  $x$  and the values calculated according to formula (2);  $\Delta^1$  the difference according to the formula (1). The latter formula fits the data more exactly than the former, as in fact the exponent  $m$  was not quite zero.

TABLE CXXXVI

Recovery of thread from an extension of 1 minute's duration to 250 mm.

$t$ (min.)	0.167	0.25	0.333	0.5	0.667	1	1.5	2	3	5	7	10	15	20	30	50
$x$ (mm.)	18.6	15.6	13.4	10.9	9.3	7.3	5.7	4.6	3.6	2.6	2.1	1.7	1.4	1.1	0.9	0.6
$\Delta$	2.0	0.6	0.2	-0.2	-0.3	-0.3	-0.2	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1
$\Delta^1$	0.7	0.0	0.0	-0.2	-0.2	-0.1	-0.1	0.1	-0.1	0.0	0.0	0.0	-0.2	-0.1	-0.1	-0.1

Concerning the relation of the course of the recovery to the amount of stretching, Kohlrausch comes to the following conclusions: The velocity coefficients or the exponents  $\alpha$  found lie between the limits 0.5 and 0.6, and, expressed as a linear function of the elongation,  $\lambda$  (elongation as a fraction of the original length),  $\alpha = 0.50 + 0.88 \lambda$ . The magnitude of the after-effect,  $C$ , increases in proportion to the load and can be expressed as  $C = 0.0383 \lambda - 0.0943 \lambda^2$ .

It is to be remarked that Kohlrausch's observations have only a very limited range, the maximal elongation employed being 13 per cent.; and, further, that, as is remarked by Kohlrausch, within this range a diminution in the growth of the amount of after-effect with the load is already noticeable.

*After-strain.*—The second set of experiments deals with after-strain. Loads of 4, 2 and 1 gram were put on the specimen, and the after-strain was followed for twenty-four hours. The elongation present at any moment is represented by  $y$ . It was found that during the first hour the after-strain was very closely expressed by formula (2), but that subsequently the calculated values approached the position of rest less quickly than the observed values. Kohlrausch thought that this deviation might possibly be due to temperature fluctuations.

In order to ascertain whether the earliest part of the stretching was also expressed by the same formula, a supplementary series of observations covering the first eighty seconds after the application of the load was made, with the result that the progress of the strain during this period was also found to be expressed by the formula (2). (Table CXXXVII).

TABLE CXXXVII

Stretching during the first 80 seconds

$t$ (sec.)	1	2	4	5	7	10	15	20	30	40	60	80
$y$ (mm.)	44.9	47.3	50.2	51.1	52.5	54.0	55.4	56.4	57.7	58.6	59.8	60.5
$\Delta$ (mm.)	0.5	+0.2	+0.2	+0.2	+0.1	0.0	0.0	-0.1	0.0	0.0	0.0	+0.2

The after-strains produced by the different loads did not follow superposable but only similar courses. The ratio of the extensions brought about by the loads 2 and 1 grams at time  $t$  as compared with the extension brought about by the load 4 grams was

$$\gamma_4/\gamma_2 = 2.16; \gamma_4/\gamma_1 = 4.41.$$

Thus the ratios of the after-strains appear as greater than the ratios of the loads. It should be remarked again that the range of extensions in question was very small, the maximum being only 7.6 per cent.

*Comparison of after-strain and recovery.*—The after-retraction following removal of the loads, 4, 2 and 1 grams was observed. The figures in the case of 4 grams may be quoted.

TABLE CXXXVIII

After-strain and after-retraction. Load, 4 g., removed after 29 hours

$t$	0.25	0.33	0.5	0.66	1	2	3	5	7	10
$y$ on extension	112.2	113.8	116.5	118.4	120.9	124.9	127.2	129.8	131.4	133.2
$x$ on retraction	119.3	—	123.0	—	126.7	130.2	—	134.3	—	137.1
$\delta$	—7.1	—	—6.5	—	—5.8	—5.3	—	—4.5	—	—3.9

$t$	15	20	30	50	70	120	200	300	400	1050
$y$ on extension	135.0	136.2	138.0	140.1	141.3	143.6	146.1	(148.6)	150.6	(156.9)
$x$ on retraction	—	139.1	—	143.3	—	146.2	—	148.6	—	—
$\delta$	—	—3.7	—	—3.2	—	—2.6	—	0.0	—	—

$t$	1260	1440	$\infty$
$y$ on extension	157.7	158.2	176.4 (calculated)
$x$ on retraction	—	151.6	—
$\delta$	—	6.6	—

$\delta$  represents the difference between  $y$ , the length on extension, and  $x$ , the length on retraction.

In the case of the loads 1 and 2 grams, the differences between the after-strain and the recovery were much smaller than those shown above. Kohlrausch concludes—"so long as the changes of length are relatively small, after-strain and after-retraction following the loading and unloading of the same weight run coincidentally." (Cf. Bouasse and Carrière later.)

*Influence of temperature on the after-effect.*—The following shows the course of the recovery at 17.3° and at 9° respectively of the rubber thread under investigation after it had been stretched for one minute by 160 mm.

TABLE CXXXIX

$t$ (min.)	0.25	0.33	0.5	0.66	1	1.5	2	3	5	7	10	15	20	30	50
17.3° $x$ (mm.)	10.5	9.1	7.3	6.4	5.0	4.0	3.3	2.6	2.0	1.6	1.4	1.2	1.1	1.0	0.8
9° $x$ (mm.)	15.9	13.8	11.4	9.8	7.9	6.3	5.2	4.0	2.9	2.5	2.0	—	—	—	—

Constants.—At 17.3°:  $C = 4.97$ ,  $a = 0.56$ ; at 9°:  $C = 7.60$ ,  $a = 0.56$ .



The curves for the two temperatures are similar to one another and show the same exponent  $\alpha$ ; but the influence of temperature on the *magnitude* of the after-effect is seen to be exactly the reverse of that found in the case of metals; that is to say, the after-effect increases with diminution of temperature.

Kohlrausch also made some observations on the effect of temperature, over the range  $7.6^{\circ}$  to  $19.5^{\circ}$ , on after-strain. He found the temperature to have a very marked effect on after-strain. In the following table is shown the after-strain, followed up to 24 hours, produced by a load of 2 grams.

TABLE CXL

Elongations (mms.).

$t$ (min.)	0.033	0.086	0.166	0.25	0.33	0.5	1	2	5	10	20	1440
$19.5^{\circ}$ . $y$ (mm.)	—	—	—	52.0	52.9	54.1	55.7	57.4	59.6	61.0	62.5	75.9
$18.7^{\circ}$ . $y$ (mm.)	—	—	49	50.9	51.7	53.0	55.0	57.1	—	—	—	—
$9.0^{\circ}$ . $y$ (mm.)	—	—	—	—	43.0	46.9	50.0	52.8	56.4	58.7	61.1	—
$7.6^{\circ}$ . $y$ (mm.)	24	28	32	33.5	35.0	37.4	41.1	45.4	49.5	—	—	—

At the higher temperatures the initial changes in the strain are greater than at the lower temperatures, but the differences in elongation at a higher and at a lower temperature diminish with increasing time. They are assumed finally to disappear. At a lower temperature a greater proportion of the total strain appears as after-strain than at a higher temperature. This observation leads Kohlrausch to remark that it is doubtful whether a division of the elastic change of form in rubber into a fore-change and an after-change<sup>1</sup> is permissible. The observation (p. 430) that the same law holds during the early seconds of stretching as later would—it may be noted—also seem to indicate that no strict distinction can be drawn between fore-strain and after-strain.

The influence of temperature on after-retraction is shown in the investigation of Wormeley into the amount of set present after a brief period of extension and a brief period of recovery. Some of the results of this investigation are shown in Fig. 21. The set is seen to be smaller at a higher temperature than at a lower one. This indicates that the effect of increased temperature on the velocity of after-retraction is similar to its effect, as revealed by Kohlrausch's work, on after-extension, *i. e.*, to increase it. The effect of increased temperature in hastening after-retraction may also be read in results obtained by Schwartz, referred to on

<sup>1</sup> Plötzliche und nachwirkende Formänderungen.

p. 470 (footnote), concerning the negative thermal coefficient of linear expansion of rubber which has previously been stretched.

*Superposition of opposite elastic after-effects.*—The peculiar character of the creep, which is designated by the term elastic after-effect, can be suggested in a striking manner by superposing, as it were, an after-effect in one direction on an after-effect in the opposite direction. The rubber after such treatment is left in a condition such that, if the preceding deformations have been suitably chosen, it will change over spontaneously from moving in one direction to moving in the opposite direction. If, say, rubber is subjected to a great or to a long-continued deformation in one sense, and shortly afterwards to a smaller or to a briefer deformation in the opposite sense, the after-effect of the latter deformation, being, as it were, fresher, will at first over-balance the after-effect of the former deformation; but after a time the older after-effect will assert itself, and the movement of the rubber will change its sign. Kohlrausch produced such a change of sign in the after-effect in torsional and (with hard rubber) in bending experiments. The results of this striking phenomenon are best shown graphically (cf. the original paper).

*Observations of Pulfrich.*—In connection with some observations (p. 494) made particularly for the purpose of deriving Poisson's Ratio\* from measurements of after-effect in rubber, Pulfrich,<sup>1</sup> working with a red rubber tube of 5 mm. internal diameter, 5 mm. wall thickness and 750 mm. in length, made some measurements of elastic after-effect, with loads ranging up to one which produced an elongation of about 150 per cent. Pulfrich found that the simple formula, (2), of Kohlrausch represented his data sufficiently well in all cases for the earlier course of the after-strain (say, up to 30 minutes), but that its subsequent course, which in some cases was followed for 4 days, could not, as Kohlrausch also had found, be represented exactly by this formula. He found also that the formula fitted his data for after-strain, even when the load had been maintained for 15 days. Studying the effect of differences, from  $\frac{1}{4}$  minute to 15 days, in the duration of the period for which the load acted, he found that the constant  $\alpha$ , which represents the velocity of recovery, fell from 0.968 after  $\frac{1}{4}$  minutes' extension to 0.167 after 15 days' extension, and could be represented by  $\alpha = rT^2$ .

Further, Pulfrich calculated from the observed change in length and change in volume of the interior of the tube the after-

<sup>1</sup> *Ann. der Phys.*, 1886, **28**, 87.

effect as it related to the lateral contraction of the tube on stretching. He found that this last could also be expressed by formula (2). In addition, he found that the exponent  $\alpha$  had the same value for the transverse as for the longitudinal after-effect.

An unsatisfactory feature of Kohlrausch's treatment of after-effect is undoubtedly to be seen in his expressing the magnitude of the after-effect at any moment as the distance which the position at that moment is removed from the final position of rest. For there is, confessedly, an element of arbitrariness in deciding on the final position of rest in any case. It is more satisfactory to express the after-effect directly in terms of the actual deformation at any time, without reference at all to the final position of rest. This is done by Phillips, and by Bouasse and Carrière. By both these last-named investigators the after-strain was found to follow a simple logarithmic law. The investigation of Phillips, which was much more limited in its scope than that of Bouasse and Carrière, may suitably be described first; although in point of date it was the later of the two.

*Law deduced by Phillips.*—Phillips<sup>1</sup> found that the total extension present at any time during the period of after-strain gave a straight line when plotted against the log. of the time. If  $x$  is the extension at a time  $t$  from the moment of applying the load, we have—

$$x = a + b \log. t,$$

where  $a$  and  $b$  are constants;  $b$  being proportional to the load, and, if  $t$  is expressed in minutes,  $a$  also being, roughly, proportional to the load.

The method of experimentation was as follows:—A strip of rubber bandage, 30 cm. long, was supported by a clip from a wall bracket; to the lower end a scale-pan and a photographic scale was attached; the scale was viewed with a telescope; a load was placed on the scale-pan, and the time was observed at which each division of the scale passed the cross wire of the telescope. The data quoted conform very closely to the logarithmic law given above. The extensions for which the observations were made were only very small; the largest, apparently, being only 3.5 per cent. of the original length. Schwartz,<sup>2</sup> however, applied the law

<sup>1</sup> *Phil. Mag.*, 1905, 9, 513. (The paper makes no mention of previous work on the subject.)

<sup>2</sup> *Loc. cit.*

to greater extensions—up to 300 per cent.—with apparently satisfactory results.

Working out the data in a number—chosen at random—of the series of observations of after-strain given by Kohlrausch, the present writer finds that the data conform almost as well to the logarithmic law as to the law given by Kohlrausch, which has been discussed above.<sup>1</sup>

The recovery from stretching at any moment Phillips finds to be a function of the time for which the load has acted, and of the time which has elapsed since the load was removed. We have the expression—

$$x = a + b \log. t - (a + b \log. t_0), \text{ i. e., } x = b \log. \left( \frac{t}{t_0} \right),$$

where, as before,  $x$  is the extension,  $b$  a constant, and  $t$  the time since the load was put on, and where  $t_0$  is the time since the load was removed.

#### THE WORK OF BOUASSE AND CARRIÈRE

The most illuminating investigation which we have on elastic after-effect in rubber is due to Bouasse and Carrière,<sup>2</sup> in which the study of after-effect is extended to greater elongations than in other investigations. It is also valuable in bringing out the influence of preceding operations on a given rubber specimen on succeeding operations. Some account of this investigation will now be given.

The rubber used was the same in all experiments; namely, a pure gum and sulphur compound, of density 0.984, in the shape of round cords 4 mm. in diameter. A fresh length of cord was taken for each experiment. The rubber was capable of being stretched to seven or eight times its original length without rupture. The load was not, as in other investigations, put on or taken off by hand, but by the movement of a platform up or down a threaded spindle. In loading, the load was gradually taken up by the rubber from the platform, as the latter moved downwards; and, in unloading, the load was gradually taken up by the platform from the rubber, as the platform moved upwards. The rate of movement of the platform could be regulated.

<sup>1</sup> And, it may be recalled, there is a certain arbitrariness in the choice of a position of rest for use in Kohlrausch's calculation.

<sup>2</sup> *Annales de la Faculté des Sciences de Toulouse*, 1903, 5 (2), 285.

The notation employed in describing the results is as follows :—

$P_0$  = the constant load on the rubber, *i. e.*, the weight of the lower clamp and attached scale, viz. 65 g.

$P_1$  = the load added.

$T_0$  = the period of time passed under the load  $P_0$ .

$T_1$  = the period of time passed under the load  $P_1$ .

$L_0$  = the length under  $P_0$ .

$L_1$  = the initial length under  $P_1$ , *i. e.*, the length at the moment the platform has descended to the point at which the load has been completely taken up by the rubber.

$L'_1$  = the final length under  $P_1$ , *i. e.*, the length after a period,  $T_1$ , of after-effect.

$\Delta_1, \Delta_2, \dots \Delta_n$  = the elongations (after-strain) under  $P_1$  in the intervals of time 0 sec., 30 sec., 1 min., 2 min., ... forming (with the exception of the first) a geometrical progression.

$\Delta$  = the total elongation (after-strain) between 30 sec. and  $T_1$ .  
(This quantity, which exceeds the readings for the first half-minute, can be determined very accurately.)

The rate of elongation during the loading, as determined by the speed of the platform, was, except where stated otherwise, 1 m. in 173 seconds. Lengths are given in units of 0.1 mm.

1. *Succession of extensions and retractions.*—The following succession of cycles with a given cord will illustrate several conclusions of Bouasse and Carrière.

TABLE CXLI

$R_1 = 500$  g.  $T_1$  (period during which after-strain was observed) = 32 min.  
 $T_0$  (the interval between successive cycles) = 0.

$L_0$	3230	3660	3700	3730	3790	3750	3790	3790
$L_1$	7500	8290	8440	8520	8660	8680	8710	8730
$\Delta_1$	24.0	10.8	9.6	9.2	9.2	9.4	8.9	9.0
$\Delta_2$	9.8	3.8	3.4	3.6	3.3	3.5	3.2	3.3
$\Delta_3$	11.1	3.8	3.5	3.5	3.2	3.6	3.6	3.5
$\Delta_4$	11.7	3.9	3.5	3.3	3.2	3.3	3.1	3.2
$\Delta_5$	11.7	4.0	3.3	2.8	2.7	2.8	2.9	2.9
$\Delta_6$	11.4	4.4	3.4	3.0	2.5	2.5	2.4	2.4
$\Delta_7$	11.2	4.9	3.6	3.2	2.4	2.4	2.5	2.3
$\Delta$	66.9	25.0	20.7	19.4	17.3	18.1	17.9	17.6
$L'_1$	8409	8648	8743	*	8930	8955	8978	8996

\* The period of after-effect ( $T_1$ ) was here 128 minutes;  $\Delta_8$  being 4.0,  $\Delta_9$  5.6, and  $L_1$  8902.

(a) In the case of each cycle the law

$$L = A + B \log. (t + \tau),$$

which, it will be observed, is substantially the same as that found later by Phillips, is found to conform to the data very much better than does the law proposed by Kohlrausch.

The data approximate to the law which Bouasse had found to hold in earlier experiments on metallic wires, viz. that the elongations observed in intervals of time which increase in geometrical progression tend to be equal. Thus, in the above experiment, it will be observed, although the interval between 16 minutes and 32 minutes is thirty-two times as great as that between 30 seconds and 1 minute, yet  $\Delta_7$  and  $\Delta_2$  differ by only one-third or one-quarter of their value.

(b) The first cycle marks itself off as very considerably different from any subsequent cycle; and, it is found, the modification which it brings about in the rubber does not disappear, no matter how long the rubber is left in repose under no load: no matter how long a rest may be allowed, no subsequent cycle duplicates the results of the first cycle. The study, discussed in the preceding chapter, of the hysteresis loops corresponding to successive cycles is in accord with this conclusion.

(c) The course of the after-strain tends to become *fixed*, as the cycles are repeated. The work on hysteresis loops discussed in the preceding chapter also showed a fixation of the cycle on repetition.

(d) Considering the fourth cycle, we see that in the eighth and ninth intervals (32-64 minutes, 64-128 minutes) the after-strains per interval are beginning to rise ( $\Delta_8 = 4.0$ ,  $\Delta_9 = 5.6$ ). Bouasse and Carrière conclude that, if the period of after-strain ( $T_1$ ) is sufficiently prolonged, the new  $\Delta$ 's will approach more and more to the  $\Delta$ 's recorded for the first cycle. This consideration would also agree with the gradual increase in the  $\Delta$ 's observed in the second cycle.

(e) The fore-strain,  $L_1 - L_0$  (and also the total length  $L'_1$ ) increases as the cycles are repeated, particularly during the first few cycles. There is at first a "loosening up," as it were, of the rubber.

The influence of the period of rest on a succession of cycles may be illustrated by the following experiment: Three cycles,  $P_1 = 500$  g.,  $T_1 = 16$  minutes,  $T_0 = 5$  minutes, were made with

each of three specimens. The specimens were then allowed to rest under  $P_0$  for the periods  $T_0$ , shown in the following table, and were then put through a second series of three cycles as before. The fore-strains ( $L_1 - L_0$ ) and after-strains ( $\Delta$ ) are given for each specimen relative to the first as 1000.

TABLE CXLII

		$T_0$					
$L_1 - L_0$	5 min.	1000	1077	1099	1110	1118	1125
	40 "	1000	1075	1096	1101	1114	1123
	24 hrs.	1000	1080	1101	1086	1115	1127
	Mean	—	1077	1099	—	1116	1125
		$T'_0$					
$\Delta$	5 min.	1000	556	501	481	468	461
	40 "	1000	549	492	598	471	455
	24 hrs.	1000	564	504	730	508	477
	Mean	—	557	499	—	—	464

If the specimens had been perfectly identical, the numbers in the first three columns (before the periods of rest) should have been identical.

It is seen that, as the number of cycles increases, the influence of the period of rest on the fore-strain becomes negligible. Thus the numbers 1110, 1101 and 1086 differ considerably and regularly; the numbers 1125, 1123 and 1127 differ little and irregularly. The case is similar with regard to the after-strain, except that the effect of the length of the period of rest appears to make itself felt to a later cycle.

2. *After-strain at different elongations.*—Although, as stated above, the course of the after-strain in the experiment first quoted can be expressed by the law,  $L = A + B \log. (t + \tau)$ , yet, owing to the circumstance that previous operations influence subsequent ones, the constants in the expression for the course of the after-strain at any one time apply only to that particular time, and not necessarily to the course of the after-strain produced by the same load at some other time. And further: the law which the after-strain follows is different for different loads. Bouasse and Carrière investigated the after-strain produced by different loads up to those giving an elongation of nearly 600 per cent. The course of the after-strain at different points of extension, taken for reference on the ordinary stress-strain curve, is singular. In the following figure is shown the total after-strain observed between 30 seconds and 32 minutes for different loads.

For reference, the stress-strain curve is also shown. The strains plotted on this curve are the total strains up to 32 minutes.

The complex character of the  $\Delta$ -stress curve is remarkable. The curve presents three points of inflexion and a maximum. The technique, of course, influences the position of these points considerably.

Not only does the magnitude of  $\Delta$  vary in this singular way, but the *course* of the after-strain also varies in an interesting manner.

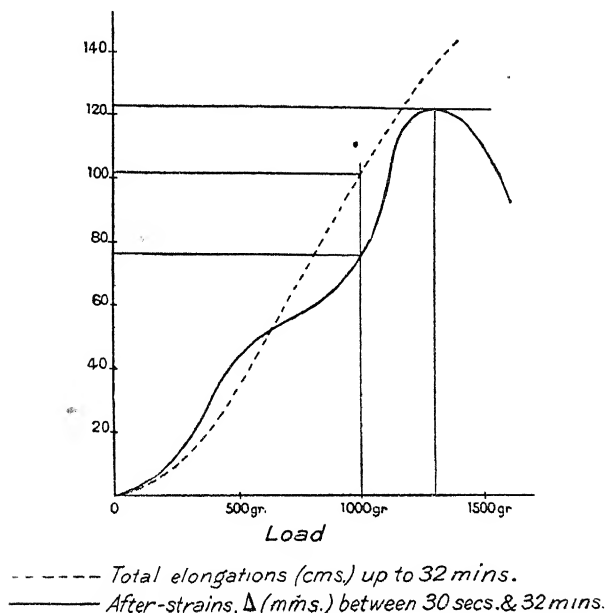


FIG. 46.

If the load is small, the increments of after-strain,  $\Delta_2 \dots \Delta_7$ , are almost constant or fall off only slightly. As the load increases, a maximum appears. With increasing loads, the maximum occurs at a later interval. Thus, for 300 g.,  $\Delta_3$  represents the maximum; for 500 g.,  $\Delta_4$ ; for 1000 g. the maximum lies beyond  $\Delta_7$ . Above 1000 g. a maximum again appears within the interval 30 seconds to 32 minutes, but, with increasing loads, moves in the direction opposite to that of its movement below 1000 g.; that is to say, it occurs at earlier intervals. Finally, when the load has been increased sufficiently—say, to 1500 g.—



the maximum has again disappeared: the  $\Delta$ 's diminish continuously from  $\Delta_2$  to  $\Delta_7$ .

Thus, it may be remarked,  $\Delta$ , the total after-strain between 30 seconds and 32 minutes, may be equal at two different loads, but may be composed in the two cases of quite different successions of  $\Delta$ 's; the  $\Delta$ 's being an increasing series for the smaller load, and a decreasing series for the larger load.

It should be remarked that, for each experiment, at the various loads investigated, a fresh specimen was used, in order to obviate the confusion of the effects of different operations.

3. *Comparison of after-strain and after-retraction.*—As mentioned earlier; Kohlrausch concluded that for small loads the amounts of after-strain or of after-retraction during a given period of after-effect were, for the same load, practically equal. But, even within the very small limits of load used by Kohlrausch, it was already becoming apparent that with the higher loads the retractions were smaller than the elongations. Bouasse and Carrière found the difference between after-strain and recovery to be very marked indeed for greater elongations. The following are some of the data obtained:—

(1)  $P_1 = 700$  g.  $L_0 = 3240$ .  $T_1 = 166$  minutes.  $L_1 = 11,030$ .  $L'_1 = 12,447$ . The interval after-effects and the total after-effect between 30 seconds and 64 minutes were as follows:—

	$\Delta_1$	$\Delta_2$	$\Delta_3$	$\Delta_4$	$\Delta_5$	$\Delta_6$	$\Delta_7$	$\Delta_8$	$\Delta$
Extension	265	111	130	139	143	144	145	146	962
Recovery	178	39	43	42	40	37	29	19	253

(2)  $P_1 = 200$  g.  $L_0 = 3210$ .  $T_1 = 64$  minutes.  $L_1 = 4150$  (elongation, 29.3 per cent.).

	$\Delta_1$	$\Delta_2$	$\Delta_3$	$\Delta_4$	$\Delta_5$	$\Delta_6$	$\Delta_7$	$\Delta_8$	$\Delta$
Extension	111	35	36	38	39	38	36	36	367
Recovery	109	16	16	16	15	12	10	7	92

4. *Influence of rate of loading.*—The speed at which a load is applied influences the distribution of the total strain between fore-strain and after-strain. Some of Bouasse and Carrière's

data on this point are as follows. Each experiment was made on a different specimen.

$P_1 = 500$  g.  $L_0 = 3230$ .  $T_1 = 64$  minutes. The actual values of  $\Delta_1$  and  $\Delta$  are given. The other  $\Delta$ 's (represented by  $\Delta'$ ) are, for purposes of comparison, given in relation to  $\Delta_1$  taken as 100. The rates at which the elongation of the specimens took place during the assumption of the load were 1 m. in 17, in 58, in 173 and in 2400 seconds.

TABLE CXLIII

	1 m. in			
	17 s.	58 s.	173 s.	240 s.
$\Delta$	954	890	780	443
$\Delta_1$	698	383	237	43
$\Delta'_2$	23	35	42	51
$\Delta'_3$	22	35	46	88
$\Delta'_4$	21	36	48	122
$\Delta'_5$	20	33	49	153
$\Delta'_6$	18	31	49	186
$\Delta'_7$	17	30	46	200
$\Delta'_8$	16	40	45	223

The general conclusions with regard to the course of the after-strain following different rates of loading were as follows: "When the rate of loading is very high, the successive  $\Delta$ 's grow less. When the rate is reduced, they increase at first and diminish afterwards. A maximum then appears, which is later, the slower the rate. Finally, for a sufficiently slow rate, the  $\Delta$ 's increase continually within the limits of the experiment."

The general conclusions arrived at with reference to the influence of the rapidity of loading on the relations between fore-strain and after-strain may be illustrated by the following experiment: After the cycles for a given specimen had become approximately fixed, the following two sets of three cycles were made; the period of after-strain in the first set being 4 minutes, and in the second set 32 minutes.  $v$  indicates a rate of elongation during loading of 1 minute per 185 seconds;  $V$  of 1 minute in 32 seconds.  $P_1 = 500$  g.  $T_0 = 5$  minutes.  $L'_0$  = the length immediately on return from the preceding cycle.  $L_0$  = the length, after  $T_0$ , at the beginning of the next cycle.  $L_1 - L_0$  = fore-strain.  $\Delta$  = after-strain.  $L'_1 - L_0$  = total elongation.

TABLE CXLIV

	$T_1 = 4 \text{ min.}$			$T_1 = 32 \text{ min.}$		
	$v.$	$V.$	$v.$	$V.$	$v.$	$V.$
$L'_0$	3353	3360	3360	3403	3420	3430
$L_0$	3213	3219	3220	3237	3251	3260
$L_1 - L_0$	4968	4922	4989	4965	5048	5016
$\Delta_2$	41	67	40	66	38	63
$\Delta_3$	47	61	46	59	43	60
$\Delta_4$	49	56	47	53	42	52
$\Delta_5$	—	—	—	47	41	44
$\Delta_6$	—	—	—	41	38	38
$\Delta_7$	—	—	—	40	37	33
$\Delta$	137	184	133	306	239	292
$L'_1 - L_0$	5105	5106	5121	5271	5287	5302

It was concluded, generally, that:—

(a) The *total* elongation tends to become the same, no matter what the rate of loading. If the rate is high, the fore-strain is smaller than if the rate is low, but it is compensated for by the after-strain.

(b) The increments of after-strain (the  $\Delta$ 's) following a high rate of loading are at first considerably larger than those following a lower rate, but tend later to become equal to them.

5. *Influence of an exceptional strain.*—The following illustrates how the behaviour of a piece of rubber may be modified by a short subsection to an exceptional strain. The extension to which the rubber in this example is being subjected normally is somewhat under 100 per cent.; the exceptional strain is to an extension of 350 per cent. The time between cycles ( $T_0$ ) is long.  $T_1 = 32$  minutes.  $P_1 = 400$  g.  $L_0 = 2570$ .

TABLE CXLV

$T_0.$	$L_0.$	$L_1 - L_0.$	After-strain.		After-retraction.	
			$\Delta_1.$	$\Delta.$	$\Delta_1.$	$\Delta.$
17 hrs. . .	2570	2200	209	463	77	128
24 „ . . .	2662	2318	159	374	91	127
24 „ . . .	2668	2342	157	353	96	123
The specimen was then stretched to 11,570 for 1 min.						
29 hrs. . .	2771	2679	168	401	91	130
17 „ . . .	2779	2641	180	411	89	142
24 „ . . .	2769	2641	171	393	97	133
7 „ . . .	2773	2677	162	371	91	128
16 „ . . .	2771	2629	177	385	91	131

The brief exceptional strain is seen to lead to an increase in the after-effect. The influence of variation in  $T_0$  is seen clearly in  $\Delta$ , which for  $T_0 = 7$  hours is 371, and becomes 385 for  $T_0 = 16$  hours. Incidentally, it may be noted, the data illustrate the conclusion, already stated, that the first cycle is markedly different from subsequent cycles, and that, within equal periods of time, the after-retraction is much smaller than the after-strain.

6. *Complete modification of the law of after-effect by a suitable arrangement of cycles.*—In the experiments described in section 2 (p. 438), from which it was concluded that the expression for the course of the after-strain changes throughout the length of the stress-strain curve, the observations at each different load were made on a different specimen of the rubber under investigation. By describing cycles at different loads with the same specimen, the course of the after-strain at any given load can be modified at will. The following experiment shows this:—

TABLE CXLVI  
 $L_0 = 3200$ .  $T_0 = 1$  min.  $T_1 = 32$  min.

$P_1$ .	$L_1$ .	$\Delta_0$ .	$\Delta_1$ .	$\Delta_2$ .	$\Delta_3$ .	$\Delta_4$ .	$\Delta_5$ .	$\Delta_6$ .
200 gms.	4000	102	30	32	34	32	32	32
300 "	4890	124	39	39	39	39	40	41
400 "	6080	146	53	55	56	57	57	58
500 "	7580	150	57	62	63	66	67	69
Then followed a period of rest under $P_0$ for 120 min.								
200 gms.	4270	90	26	26	28	26	24	23
300 "	5210	111	38	35	35	32	31	31
400 "	6440	130	43	46	43	42	41	41
500 "	7850	120	46	49	49	49	49	50
400 "	6690	110	39	36	30	24	18	16
300 "	5500	106	28	25	17	6	0	-2
200 "	4570	72	16	10	2	-3	-9	-10
Then followed a period of rest under $P_0$ for 840 min.								
200 gms.	4250	97	29	30	29	28	27	21
300 "	5190	122	38	38	35	35	32	31
400 "	6450	129	45	46	43	41	40	40
500 "	7870	126	43	48	47	46	46	45

The influence of the superposition of after-effects is clearly seen in this series of cycles. In two of the cycles the after-strain actually changes its sign.

The following experiment also illustrates strikingly the influence

of a previous extension upon a subsequent one. Five specimens of the rubber cord were taken, and were subjected first to a load of 500 g. for different periods of time ( $T_1$ , given at the head of the table); and a load of 300 g. was put on as soon as the load of 500 g. had been removed.

TABLE CXLVII

Load.		$T_1 = 0$ min.	16 m.	32 m.	128 m.	760 m.
500 g.	$L_1 - L_0$ (Fore-strain) .	4280	5465	4490	4980	5620
"	$L'_1 - L_0$ { (Fore-strain+ After-strain) }	4280	6181	5340	6089	6928
No load	$L'_0 - L_0$ .	230	390	390	480	590
300 g.	$L_2 - L_0$ (Fore-strain) .	2030	3110	2510	2950	3590
"	$(L_2 - L_0)/(L_1 - L_0)$ .	0.474	0.568	0.559	0.590	0.638
"	$(L_2 - L_0)/(L'_1 - L_0)$ .	0.474	0.503	0.470	0.483	0.518
"	$\Delta_1$ . . . . .	87	80	82	79	92
"	$\Delta_2$ . . . . .	22	21	16	20	22
"	$\Delta_3$ . . . . .	22	18	10	8	17
"	$\Delta_4$ . . . . .	24	12	2	4	10
"	$\Delta_5$ . . . . .	29	9	0	3	0
"	$\Delta_6$ . . . . .	35	11	0	-1	-7
"	$\Delta_7$ . . . . .	35	15	0	-4	-13
"	$\Delta_8$ . . . . .	39	21	6	-7	-17
"	$\Delta_9$ . . . . .	43	—	—	-3	-16
"	$\Delta_{10}$ . . . . .	—	—	—	3	—

Considering first the after-strain under the 300 gram-load: it will be seen that with  $T_1 = 0$  minute a minimum shows itself in the increments of after-strain, but is not very marked; with  $T_1 = 16$  minutes the minimum is very clear; and with  $T_1 = 32$  minutes the after-strain during three succeeding intervals is 0. When the time for which the first load (500 g.) has acted is 128 minutes, the after-strain with the second load (300 g.) shows two points of inversion; and it appears probable that, if the observations were to be carried far enough, all values of  $T_1$  greater than 128 minutes would show two points of inversion. The first inversion is, clearly, due to the influence of the after-retraction deriving from the previous loading (with 500 g.); the second point of inversion to the after-strain deriving from the second loading (with 300 g.) asserting itself.

Considering the fore-strains, which indicate the position of the second loading curve: the influence of  $T_1$  on them is obvious from an examination of the ratios of the fore-strains under the two loads, *i. e.* the ratios  $(L_2 - L_0)/(L_1 - L_0)$ . The mean value of

this ratio is 0.566; the differences from the mean are  $-0.092$ ,  $+0.002$ ,  $-0.007$ ,  $+0.024$ ,  $+0.072$ .

Some data given by Cantone and Contino,<sup>1</sup> in a study of torsion in rubber, bring out the influence of previous torsions on subsequent ones.

#### DECAY OF TENSION AT CONSTANT ELONGATION

Another phase of the question of elastic after-effect is the secular diminution of the force required to hold a piece of rubber at a given fixed extension. Measurements of this were first made by Phillips.<sup>2</sup> The experimental arrangement was as follows: A balance was so arranged that the beam was just lifted off its supports; the scale-pan was removed from one end of the beam; and between this end of the beam and a firm base a strip of the rubber bandage under experiment was fastened. Weights were put on the other pan, so as just to balance the tension of the rubber. The weights were altered from time to time, as the tension decayed. As the beam of the balance was only just raised above the supports, the elongation of the rubber was practically constant all the time. Schwartz<sup>3</sup> mentions that the top grip is conveniently rested initially upon a horizontal support; at each reading, the requisite weights being put on the balance-pan to raise the grip just clear of its support.

In the case given by Phillips, the tension diminished from 1472.5 g. at 1 minute 30 seconds to 1384.5 g. at 1436 minutes. The decay of the tension followed a logarithmic law; the tension,  $S$ , at any time,  $t$ , being given by  $S = a - b \log. t$ , where  $a$  and  $b$  are constants;  $b$  was found to be proportional to the elongation. After the first day, the decay of tension was more rapid than would be calculated from the above expression.<sup>4</sup>

Schwartz<sup>5</sup> made experiments on the diminution of tension, with two rubber samples containing respectively 88 and 66 per cent. of pure (Para) gum, at temperatures between 120° and 200° F. (49° and 93° C.); the constant extension maintained being 100 per cent. Under these conditions the tension-time curves were

<sup>1</sup> *Rend. First Lomb.*, 1899, 32 (2), 189 (*Fortschr. Phys.*, 1899, I, 502).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.*

<sup>4</sup> In the case of the experiment for which the first day's limiting figures are mentioned above, the tension after twelve months had fallen to 22 grams. For an observation of possible significance in this connection, *vide* Goulier, *Les Mondes*, 1869, 20, 11.

<sup>5</sup> *Loc. cit.*

found to follow the logarithmic law only approximately. Schwartz made a few observations, at ordinary temperature, on the relation of the decay of tension at constant elongation to the state of cure. More extensive experiments, however, are, as Schwartz points out, to be desired in this connection.

Schidrowitz<sup>1</sup> expresses the opinion that the determination of the decay of tension at constant elongation is a test that should prove of great utility. The test is also thought by the Bureau of Standards<sup>2</sup> to be, under specified conditions, "indicative of the quality of the rubber and the extent of vulcanization." An apparatus for conducting a decay-of-tension test is described by Douty.<sup>3</sup> In this apparatus a number of specimens, each attached to a spring dynamometer, are stretched in a frame, and the decrease of tension is read off at any chosen interval.

#### ELASTIC AFTER-EFFECT AND THE EVALUATION OF RUBBER

Tests involving after-effect, made on rubber for the purpose of evaluating its quality, have almost invariably dealt with after-retraction or recovery from stretching, and have taken the form of determinations under specified conditions of sub-permanent set. It is not impossible, however (see *infra*), that tests dealing with after-extension would be more satisfactory and convenient.

Almost the only observations available in which a comparison of a number of rubber samples is made in regard to after-extension are a few made by Schwartz.<sup>3</sup> Test pieces,  $\frac{1}{4}$  in. wide throughout and 3 in. clear between the grips, were loaded with a 2-lb. weight; and, after one minute had been allowed to elapse, readings of the after-extension up to 10 minutes were made by means of a cathetometer.

As already mentioned (Phillips, p. 434), the extension in a given time,  $t$ , is given by  $x = a + b \log. t$ , where  $a$  is the initial extension in the first minute. It is convenient to start the readings after one minute, as this gives the zero on the log. time scale for the after-extension curve. As the results follow a straight line law, it was found sufficient to take 4 or 5 readings only at time intervals of 2 or 3 minutes. Four rubber samples

<sup>1</sup> *Rubber*, London, 1911, p. 237.

<sup>2</sup> *Bureau of Standards Circular*, No. 38, p. 35. Also Douty, *Rubber Industry*, 1914, p. 239.

<sup>3</sup> *J. Inst. Elec. Eng.*, 1910, 44, 693. Cf. Memmler, *Rubber Industry*, 1911, p. 358.

of different quality gave the following values for the constants  $a$  and  $b$ .

TABLE CXLVIII

Compound.	$a$ .	$b$ .
60 per cent. rubber . . .	30.5	2.5
50 " " " . . .	13.8	1.0
40 " " " . . .	8.9	0.6
30 " " " . . .	4.0	0.3

The composition of the non-rubber portion of the above compounds is not stated; but it appears that the compounds represented some of those (No. 1379, etc.) mentioned on p. 419. The after-extension test on these samples placed them in the following order: Nos. 1379, 1381, 1382, 1389—a considerable gap here—1390, 1392, 1391; that is to say, when the amount of after-extension was plotted against  $\log t$ , the lines obtained increased in inclination in this order. This order may be compared with the order in which the breaking figures placed the same samples, with the order in which the sub-permanent set placed them, and with the order in which the cyclic test placed them (*vide* Table CXXXII, p. 419).

The following points may be noticed as favouring an after-extension test as compared with the more usual after-retraction or sub-permanent set test:—

(a) The after-retraction following extension under a given load is, as shown by Phillips (p. 435), a function of the extension. As determined in the ordinary set tests, the after-retraction in question is that following on extension to a constant *length* and not under a constant load. The presumption is, however, that under these conditions also after-retraction is a function of the extension.

(b) Whereas set tests, as most generally laid down, occupy from several hours to one day or more, the after-extension test, as employed by Schwartz, occupies only 10 minutes.

(c) As—it would appear—the rubber need not be subjected to very severe strain in conducting the after-extension test, it might possibly be feasible, at the close of the test, to use the same test-piece for some other test without serious error.

(d) Since several observations are made in the after-extension test, whereas only a single observation is made in the ordinary



set test, errors in individual observations are less important in the former than in the latter case.

*Sub-permanent set.*—In performing a set test, the rubber is held under tension, for a specified period of time, either under a fixed load or, as is more usual, at a fixed extension;<sup>1</sup> it is then released, and, after a given interval of rest, the distance of the rubber from its original length is measured. The Bureau of Standards<sup>2</sup> specifies as the period of tension 1 to 10 minutes and an equal interval as the period of rest; and in tests actually recorded<sup>3</sup> the intervals were 1 minute only. For the highest-grade rubber it would seem that, at all events for the extensions usually employed in making set tests, these intervals are too small for accuracy. In what is known as the Admiralty test, and in set tests as employed by the majority of investigators who have published results on the subject, the period of tension and of rest are much longer than those mentioned above. Beadle and Stevens measured set after extending the specimen for 24 hours to a length of 400 per cent., and giving 6 hours for recovery. For a comparison of results obtained in this way with the breaking figures, and with the results of cyclic tests on the same samples, Table CXXXII (p. 419) may be examined.

The test-pieces employed by Beadle and Stevens were prepared from strips, 5 mm. wide and 1 mm. thick, by punching two holes, 100 mm. apart, and cutting away the rubber between the holes, so as to produce a sort of elongated ring. Other investigators have employed for set tests the rings used on the Schopper tensile testing machine. The rings are stretched, say, over a glass plate, which may be tapered at the upper corners to allow of the rings being put on with ease, of such a size that the rings are extended to, say, 500 per cent. of their original length. A convenient arrangement for stretching twenty rings at any

<sup>1</sup> As Schidrowitz (*Rubber Industry*, 1911, p. 244) points out, it is not satisfactory to fix the tension under which the rubber is to be held in a set test as a definite percentage of the breaking stress—as is done, *e. g.* in the tests by Memmler and Schob, Mitt. Prüfungsamt, 1909, 27, 173—particularly if it is desired to compare rubber samples of different types. “In stressing a high-grade rubber to a definite percentage of its breaking-stress, the absolute load applied, and therefore the absolute work done in the rubber are far greater than in the case of a low-grade material.”

It would appear to be difficult to fix the tension satisfactorily, either on a load or on an elongation basis, in order to compare rubbers of different types satisfactorily in a set test. In the case of rubbers of the same type—as, say, plantation samples cured in the same mix—it seems fairly satisfactory to compare the rubbers by extension to a fixed percentage length.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Douty, *loc. cit.*

desired constant length up to 1000 per cent. is described by Eaton.<sup>1</sup> After remaining stretched for 24 hours, the rings are removed, and their elongation is measured after a rest of 6 hours.

It cannot be said that this procedure is entirely satisfactory for the conduct of set tests. (a) The ring is under a greater strain over the edges of the glass plate than at other points. (b) Slight inequalities in the breadth of the ring or a slight unevenness of its inner surface may lead to errors. (c) The measurement of the length of the test-piece before and after the stretching is a somewhat unsatisfactory operation in the case of rings. It is necessary to put the ring under a certain amount of tension in order to "straighten it out." The load employed for this purpose is, of course, not large—de Vries and Hellendoorn employed 200 g. for rings  $3.75 \times 5$  mm. cross section<sup>2</sup>; but it does not seem to be entirely desirable that the rubber should be subjected to any fresh stretching after the actual set-producing stretching; and, further, the after-extension following this fresh stretching tends to make difficult exact readings of length. The apparatus employed for measuring the length of the rings is the Martens-Schopper apparatus.

It would seem that the investigation of set demands a higher order of exactness in reading the deviation from the undeformed dimensions of the test-piece than has hitherto been employed. Indeed, it must be concluded, generally, that elastic after-effect, in its relation to the quality of rubber, has not been investigated as closely or as fully as could be desired.

A collection of 306 samples of latex crêpe, which had been vulcanized according to the Delft Institute's standard procedure (p. 362), were examined for set after being stretched for 24 hours to a length of 400 per cent., and then allowed a period of rest of 6 hours. Van Rossem<sup>3</sup> examined the results statistically in relation to the vulcanization coefficients of the samples, and found the following negative coefficient of correlation:  $r = -0.772 \pm 0.016$ . The degree of correlation is somewhat less than that found by the same workers for the relation of the other mechanical properties examined, such as the elongation at break, to the vulcanization coefficient; but, having in mind the comparatively inexact character of the test, it may be considered that the correlation between increasing vulcanization

<sup>1</sup> *Dept. Agric. F.M.S. Bull.*, No. 27, 1918, p. 22.

<sup>2</sup> This would produce an elongation of, say, 5–10 per cent.

<sup>3</sup> *Loc. cit.*, pp. 115, 154; *Delft Communics*, p. 171.

coefficients—representing, broadly, advancing states of cure—and decreasing set was of the same order in this collection as was the correlation between the vulcanization coefficient and other tensile properties. It is concluded from this by the Delft Institute that the determination of set cannot give any further information, for the purpose of evaluating rubber, than that which will be given by other tensile tests, such as the stress and elongation at break and the stress required to produce a given length.

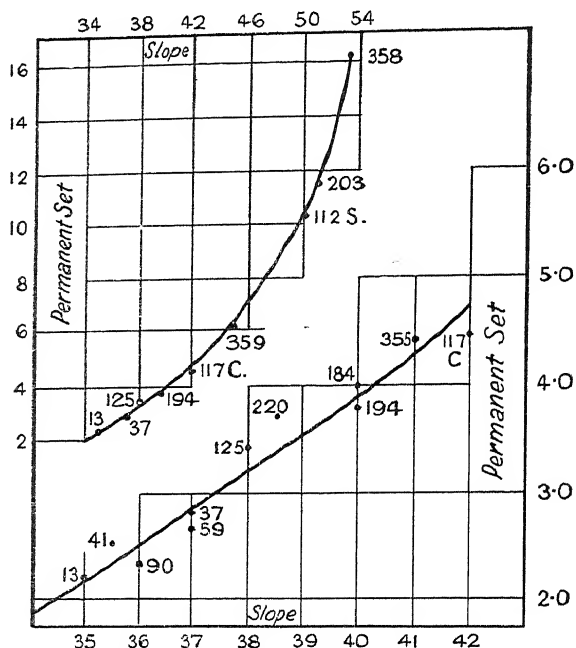


FIG. 47.<sup>1</sup>—Relation between set and "slope," or "type," for a number of samples.

The results of the statistical treatment of the data for the collection of samples in question does not, however, seem to be a sufficient ground for such a sweeping conclusion. A careful examination of individual cases would seem to be desirable.

*Relation of sub-permanent set and "slope."*—De Vries and Hellendoorn<sup>2</sup> have examined the relation of set to the "slope" of the stress-strain curve. By "slope," as explained elsewhere

<sup>1</sup> From the *Journal of the Society of Chemical Industry*.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1917, **36**, 1258.

(p. 349), is meant the inclination of the "flat," final portion of the stress-strain curve. Samples consisting of 92.5 parts of rubber and 7.5 parts of sulphur were vulcanized at 148° for various periods of time. From each vulcanized slab a number of rings were used for the ordinary test (stretching to break) on the Schopper machine, and a number were used for determinations of set. For the latter purpose, the length of the rings (rings 44.4 mm. internal diameter) was measured under a small fixed load (200 g.); the rings were then stretched to five times their original length for 24 hours; and, after a rest of 6 hours, their length was measured again as before. In the first instance fifteen samples, including rubbers of different kinds,<sup>1</sup> were examined at three or four different states of cure. For each rubber the set corresponding to de Vries' standard state of cure (*i. e.* the cure giving a stress-strain curve passing through the position 990 per cent. at 1.30 kg./mm.<sup>2</sup> load) was obtained by interpolation. A close relationship was found between the set and the "slope" of the stress-strain curve. The curve connecting the two quantities was almost a straight line within the range of slopes of most general occurrence, as may be seen from the figure on p. 450.

The following table shows the average relation found between set, as a percentage of the original length, and slope.

TABLE CXLIX

Slope . . .	34	35	36	37	38	39	40	41	42
Set . . .	1.9	2.2	2.53	2.87	3.2	3.54	3.9	4.3	4.75

A further number (thirty-eight) of samples were examined for set at one state of cure; a correction being applied to obtain the set for the standard state of cure. All the samples prepared according to the ordinary plantation procedures conformed to the relationship already found. There were, however, among thirty-eight samples, nine samples which did not so conform. And it is interesting to note the nature of these exceptional samples. Five were not acetic acid samples, but had been prepared by the use of sulphurous acid as a coagulant. The deviation in the case of these samples was not very large. The other four exceptional samples showed a considerable deviation from the relationship previously found between set and slope. They consisted of matured coagulum ("slabs"), imitation Para ball or very thick

<sup>1</sup> Latex crêpe, lump crêpe, scrap crêpe, bark crêpe, smoked, washings, imitation Para ball.

crêpe, *i. e.* rubber containing a higher proportion of serum solids than ordinary plantation crêpe or sheet. These samples showed a considerably greater amount of set than their low slope would have indicated.

De Vries and Hellendoorn concluded that, as slope can be ascertained directly from the stress-strain curve, it is superfluous, in the cases of ordinary samples of plantation rubber, to make a separate test for set.

## CHAPTER XX

### RELATION OF THE THERMAL, OPTICAL AND ELECTRICAL TO THE MECHANICAL BEHAVIOUR OF RUBBER

#### THERMAL AND MECHANICAL RELATIONS

THE mutual relations of thermal and mechanical effects in rubber deserve examination, not only because, in regard to the technical applications of rubber, such relations are probably of great practical importance, but also because, in regard to the problem of the intimate physical constitution of rubber, an understanding of certain striking aspects of these relations would not improbably be very illuminating. Interest in the thermo-elastic relations of rubber has centred round the paradox sometimes known as the Joule Effect. This challenging effect is as follows: when a strip of stretched rubber, one end of which is free, is warmed, the effect of the heat is to bring about a contraction. Associated with this paradoxical behaviour is the abnormal character of the thermal effect of stretching rubber; for, contrary to the behaviour of most bodies, rubber becomes warmed on being stretched.

The behaviour of rubber in these respects was first remarked as long ago as 1805, when Gough<sup>1</sup> recognized, by holding a strip of rubber to his lip before and after stretching it, that stretching increased its temperature.<sup>2</sup> Gough also observed that, if a strip of rubber was extended vertically by means of a weight attached to the lower end, it became shorter when heated and longer when cooled. Page<sup>3</sup> in 1847 reported, independently, similar observations. Joule,<sup>4</sup> who at the time was unaware of

<sup>1</sup> *Memoirs Manchester Lit. and Phil. Soc.*, 1805, 1 (2), 288; *Nicholson's Jour.*, 1806, 13, 305.

<sup>2</sup> Thomson in his *System of Chemistry* (Vol. V, Edinburgh, 1807) tells us that Gough had been blind from an infant, and hence that his sense of touch was particularly delicate.

<sup>3</sup> *Amer. Jour. Sc. and Arts (Sillman's)*, 1847, 4 (2), 341.

<sup>4</sup> *Proc. Roy. Soc.*, 1857, 8, 355; *Phil. Mag.*, 1857, 14 (4), 226; *Joule's Scientific Papers*, I, 405.

these earlier observations, found that, while metals and other materials which he investigated were cooled by being stretched, rubber, on the contrary, was warmed; and Thomson (Kelvin) predicted, on theoretical grounds, that, in view of this fact, stretched rubber would contract on being heated. Joule<sup>1</sup> confirmed this prediction experimentally, and made a series of quantitative measurements in regard to the phenomenon.

*Thermal effects of mechanical deformation.*—The following Table shows the results which Joule obtained with a strip of vulcanized rubber  $\frac{3}{8}$  in. square. The temperature change was determined by means of a thermo-electric junction placed in an orifice through the centre of the strip. The elongation was measured between two pins originally 4 inches apart.

TABLE CL

Length (ins.)	4	4.06	4.12	4.3	4.8	5.2	5.87	6.6	7.25	7.75
Thermal effect (°C)	0	-0.003	-0.004	-0.004	-0.001	0.014	0.053	0.095	0.137	0.187

At the outset a small cooling was observed. Similar results were obtained with a strip of raw rubber. Joule reported that the effect on extension was not sensibly different, except of course in sign, from that on retraction. Villari,<sup>2</sup> however, considered the warming effect on extension to be greater than the cooling effect on retraction; and subsequent measurements have confirmed this view. Thus, Bjerkén<sup>3</sup> found the following changes in a rubber band 33 mm. in diameter (width and thickness not stated).

TABLE CLI

Elongation (mm.)	20	40	60	80	100
Thermal effect (°)					
On stretching	0.016	0.052	0.10	0.174	0.316
On retraction	-0.0095	-0.022	-0.047	-0.107	-0.193

The experiment of Joule mentioned above was conducted at 7.8°. Joule stated that, if the temperature were a little higher, the initial cooling was not observable. Schwartz and Kemp,<sup>4</sup>

<sup>1</sup> *Phil. Trans.*, 1859, **149**, 91; *Joule's Scientific Papers*, I, 413.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Ann. der Phys.*, 1891, **43**, 817.

<sup>4</sup> *Mem. Manchester Lit. and Phil. Soc.*, 1911, **55**, No. XII; *Jour. Munic. Schl. Technology, Manchester*, 1911, **4**, 221.

working at  $0^{\circ}$ , have examined more closely the initial cooling which occurs when the rubber is at a low temperature. They inserted ten thermo-electric junctions along the length of a test piece (6 in.  $\times$   $\frac{1}{4}$  in. square) consisting of a rubber compound containing 88 per cent. of pure (Para) gum. They found the cooling effect to be maximal (value,  $-0.0017^{\circ}$ ) at an elongation of 0.095 cm. and to pass into a heating effect (value,  $+0.0004^{\circ}$ ) at an elongation of 0.193 cm. They found that the initial cooling effect on extension lasted over a greater range for a piece of spread rubber tape than for the above-mentioned sample. This was interpreted as indicating the effect of age (? hardening) in the sample.

*Chauveau's view of the molecular mechanics of the phenomena.*—Chauveau,<sup>1</sup> who sets out his results in a number of graphs, also found the cooling on retraction to be considerably smaller than the heating on extension. He found, corresponding to the slight initial cooling on extension, a slight heating on recovery from small extensions. Further, he found that the rate of extension has a marked influence on the magnitude of the thermal effect; a high rate resulting in the disappearance of initial cooling and increasing the amount of heating at any given point. The character of the loading also was found to influence greatly the magnitude of the thermal effect; the amount of heat produced by step-wise loading to a given extension being very much less than that produced by extension under the same load at one step.

Chauveau views the thermal effect of deformation in rubber as the resultant of (a) the effect of the displacement of the molecules in relation to one another, (b) the effect of a change of dimensions of the intermolecular spaces. On extension, the result of (a) is to produce heating, and of (b) to produce cooling; on retraction, the result of (a) is to produce cooling, and of (b) to produce heating; on compression, both (a) and (b) produce heating. Schwartz and Kemp adopt this view. The initial cooling observed on extension at low temperatures is attributed by them to the work which has to be done on the rubber in order to break up a weak type of molecular grouping, which, at a higher temperature, breaks up at the first application of the stress or is possibly unstable altogether at the ordinary room temperature.

*A neutral point.*—As will be pointed out shortly, Lundal<sup>2</sup>

<sup>1</sup> C. R., 1899, 128, 388, 479.

<sup>2</sup> Ann. der Phys., 1898, 66, 740.



found that, if a stretched piece of rubber were subjected to increasing temperatures, there was, for a given load, a temperature (the point of inversion) at which contraction of the rubber ceased to occur, and above which extension took place. The point of inversion was higher, the greater the load on the rubber. Regarding the thermal effects of stretching in the light of this result, it was concluded that, for rubber held under a given load, there should be a temperature at which the addition of the load in question would produce no thermal effect in the rubber and above which it would produce cooling; or, conversely, that, for a given temperature, there would be a load at which no thermal phenomena would appear. Lundal found this conclusion to be confirmed experimentally. He obtained for a sample of black rubber thread, of specific gravity (at  $17.4^{\circ}$ ) 0.90166, and of cross section 0.042 cm.<sup>2</sup>, the following figures:—

TABLE CLII

$t$  = the temperature ( $^{\circ}$ ).  $P$  = the load (grams), at which no thermal phenomena were observable.

$t$ .	18.0	29.9	37.0	48.0	58.0	46.2	38.3	29.9	18.8
$P$ .	44.5	75.0	83.6	96.6	102.2	88.0	85.5	60.7	43.2

In this connection it may be observed that Joule had found in an experiment on a rubber ring, the extension of which was continued to the breaking-point, that—excluding the last two figures—the thermal effect, after reaching a maximum, fell off when the extension was carried further, as the following table shows.

TABLE CLIII

Initial length = 3.3 in. Increments of load as indicated.

Additional load (lb.)	2.5	2	2	2	2	2	2	4	2	4	4
Length after addition of load (in.)	6.8	10.9	14.6	17.6	18.5	19.4	20.1	20.9	21.3	22.0	Broke
Thermal effect ( $^{\circ}$ )	0.110	0.242	0.330	0.132	0.088	0.068	0.004	0.001	0.009	0.004	

#### EFFECT OF HEAT ON STRETCHED RUBBER

*Joule's observations.*—The following table shows the amount of contraction observed by Joule on heating a sample of vulcanized rubber, of specific gravity 0.99, and of cross section  $\frac{3}{8}$  in. square, stretched by the loads shown. At each load the length of the specimen was read at four temperatures, mostly ranging from about 0 to  $50^{\circ}$ . At small extensions, heating produced, not contraction, but expansion.

TABLE CLIV  
Initial length = 4 in.

Load (lb.)	7	14	21	28	35	42
Mean elongation (roughly)	4.5	4.9	5.45	6.25	7.25	8.4
Linear expansion with rising temperature <sup>1</sup>	$\frac{1}{9009}$	$\frac{1}{5093}$	$\frac{1}{2435}$	$\frac{1}{1360}$	$\frac{1}{814}$	$\frac{1}{656}$

It will be seen that the amount of contraction increased with increased load. Similar results were obtained by Joule with samples of raw rubber.

Bjerkén<sup>2</sup> could observe no stage of expansion. He found contraction to occur on heating stretched rubber, even when the rubber was under small loads only. (The character of the rubber used is not stated.) In his experiments, the linear movements of the rubber on heating were magnified by means of a mirror, to which movements of the wire passing between the rubber strip and the loading weight were communicated. The following table shows the results which were obtained over a temperature range of 18°–22°.

TABLE CLV

$L_0$ , the original length of the rubber = 33 mm.  $\delta L/\delta \theta$  = the change of length per degree, expressed in scale divisions (1 scale division = 0.0106 mm.).

Load (gms.).	Length (mm.), $L$ .	Elongation (per cent.).	$\delta L/\delta \theta$ .	$\frac{1}{L} \cdot \frac{\delta L}{\delta \theta}$ .
50	36.0	10	— 0.4	— 0.0312
200	49.9	50	— 1.5	— 0.0332
350	77.3	130	— 3.7	— 0.0351

$\frac{1}{L} \cdot \frac{\delta L}{\delta \theta}$ , the change of length per degree per unit length, is seen to increase with increasing load.

Bouasse has also made some observations, given in Table CLXIII (p. 469), on the contraction of stretched rubber when heated. At a load corresponding to an elongation, at 15°, of 28 per cent., the contraction on heating to 46° was 1.4 per cent. of the original

<sup>1</sup> For calculating the length corresponding to a given temperature, Joule took the mean of the length during the period of rising temperature and of the length during the period of falling temperature. Undoubtedly, this is not a permissible procedure. Hence Joule's figures, which are quoted here because of their historical interest, are to be regarded as giving merely a rough view of the course of the phenomena. (Cf. Bouasse and Carrière, pp. 352–3.)

<sup>2</sup> *Loc. cit.*, pp. 819–21.

length; at a load corresponding to an elongation, at 15°, of 447 per cent., the contraction on heating to 46° was 45.9 per cent. of the original length.

*Lundal's observations.*—Lundal,<sup>1</sup> as a result of studying the amount of contraction under different small loads over a range of temperatures from 3°–72.3°, arrived at the following conclusions:—

(a) The effect of increasing the temperature in producing contraction is greater at lower temperatures than at higher ones. (Joule's figures may be seen to be in agreement with this conclusion.)

(b) If the temperature is raised sufficiently, contraction no longer takes place, but expansion occurs.<sup>2</sup>

(c) The temperature at which the change of sign occurs is higher, the greater the load.

The rubber used by Lundal was black rubber thread of specific gravity 0.90166 at 17.4°. Numerical results are shown in the following table:—

TABLE CLVI

$\Delta$  = the expansion in scale divisions.  $\alpha \cdot 10^6$  = the coefficient of linear expansion (in scale divisions) over the interval. P = load (gms.).  
 $L_P$  = length under load P.  $Q_P$  = cross-section under load P.

1. P = 20.3. $L_P = 10.67$ cm. <sup>1</sup> $Q_P = 0.04065$ cm. <sup>2</sup>									
Temperature	3.0	17.8	34.4	45.0	58.2	70.3			
$\Delta$	—0.1	8.5	8.3	18.5	16.4				
$\alpha \cdot 10^6$	18.6(?)	52.8	68.4	108.2	103.8				
2. P = 30.3. $L_P = 11.13$ cm. $Q_P = 0.03900$ cm. <sup>2</sup>									
Temperature	3.3	18.3	34.3	45.0	59.2	72.3			
$\alpha \cdot 10^6$	—55.4	—23.8	—4.0	36.9	81.9				
3. P = 40.3. $L_P = 11.42$ cm. $Q_P = 0.03802$ cm. <sup>2</sup>									
Temperature	5.1	18.6	35.1	45.3					
$\alpha \cdot 10^6$	—158.5	—103.3	—74.0	—49.6					

The original, unstrained length would appear to have been approximately 10 cm.

*Points of inversion.*—We may thus distinguish points of inversion, under different conditions, as follows:—

(a) For rubber at low temperatures—7.8° in Joule's experiments; 0° in Schwartz's—there is a point of inversion, in regard to the load, at which the effect of slightly raising the temperature changes over from an expansion to a contraction.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> This had already been remarked in 1867 by Govi (*loc. cit.*).

(b) For rubber under small loads—corresponding, say, to not more than 20 per cent. elongation—there is a point of inversion, in regard to increasing temperatures, at which the temperature ceases to produce a contraction and produces an elongation.

A point of inversion of the former kind is no longer recognizable if the initial temperature of the rubber is as high, say, as ordinary room temperature; and a point of inversion of the latter kind would—it is suggested by the data given by Lundal—no longer be recognizable within a feasible range of temperatures at moderately large elongations (say, 25 per cent.).

It would appear, then, that the conditions under which linear expansion and points of inversion may occur on heating stretched rubber are very limited. In the majority of conditions, the application of heat to stretched rubber brings about linear contraction. And it is this last paradoxical behaviour that will now be examined more closely.

#### CAUSE OF THE JOULE EFFECT

*Govi's suggestion.*—The first suggestion offered in explanation of the Joule Effect was that of Govi,<sup>1</sup> who regarded rubber as “a sort of solid foam composed of innumerable vesicles full of gas.”<sup>2</sup> When rubber is stretched, he supposed, the vesicles lengthen in the direction of the extension and become contracted in the perpendicular direction. On the application of heat, the gas in the vesicles would expand, and each vesicle would endeavour to return to its original spherical form. This would lead to linear contraction and transverse expansion of the rubber.

Experiments described by P. Thomas<sup>3</sup> and by Hesehus<sup>4</sup> may be considered as sufficiently disposing of this conception. Thomas took the specific gravity (0.91370) of a sample of rubber. He then dissolved the rubber in carbon bisulphide, and recovered it by spreading out the solution in successive thin layers. This procedure may be assumed to get rid of any gas bubbles in the rubber: yet the recovered material had a specific gravity (0.91320) identical with that of the original material. Hesehus pointed out that, on Govi's hypothesis, a stretched rubber strip should shorten if the external pressure were reduced. He stretched a rubber strip 0.5 m. long and 6 mm. thick to double its length;

<sup>1</sup> *Atti. R. Accad. Torino*, 1867, **2**, 225, 455; *Les Mondes*, 1869, **19**, 640.

<sup>2</sup> *Un corps bulleux*.

<sup>3</sup> *Les Mondes*, 1869, **20**, 7.

<sup>4</sup> *J. Russ. Phys. Chem. Soc.*, 1883, **14**, 320 (*Fortschr. Phys.*, 1883, **I**, 350.)

left it in repose in a vertical glass tube for several days, and then evacuated the tube. No change in length took place.

More recently Fessenden has suggested that the changes of temperature in rubber produced by extension and contraction and also the Joule Effect are explicable on the view that rubber is composed of fluid portions enclosed in solid envelopes (*vide* Chap. X, p. 257). Fessenden's conception of the structure of rubber does not, however, include the impermissible assumption of gas-filled vesicles. In his conception, the fluid in question is not gas but a viscous liquid.<sup>1</sup>

*Suggested increase of the modulus of elasticity.*—Schmulewitsch<sup>2</sup> advanced the solution that the result which became apparent on heating a piece of stretched rubber represented the algebraic sum of two effects—namely: normal thermal expansion, acting to lengthen the rubber, and increase in Young's modulus, acting to shorten the rubber. At small loads, it was conceived, the former effect overbalanced the latter. Thus, in this view, the Joule Effect did not imply a negative coefficient of thermal expansion: the thermal expansion was normal; the abnormal feature in the Effect was an increase in the elastic modulus with increase of temperature. (The effect of increase of temperature is, in the case of all other materials examined, to reduce the elastic modulus.) An increase in the modulus would mean that the same load would no longer be able to produce as great an extension as it did before.

*Schmulewitsch's demonstration of the Joule Effect.*—In support of this view, Schmulewitsch quoted two experiments, which he supposed to prove the posited increase of the modulus with increase of temperature, but which, in fact, cannot be regarded as more than mere demonstrations of the Joule Effect under a slightly different aspect from that examined by Joule. These demonstrations were as follows:—

1. One end of a rubber thread was fastened to the bottom of a long, narrow, metal cylinder, into which, for the purpose of raising the temperature, water could be poured. The other end was connected with a length of catgut, which led over a roller to a resonance box. The end of the gut was fixed. Water

<sup>1</sup> It may be remarked that this conception of a continuous solid phase enclosing or containing a liquid phase, is substantially similar to that held of other gels, which, like rubber, become anisotropic when deformed, and in their stretched state show a negative coefficient of linear expansion.

<sup>2</sup> *Vierteljahrsschrift der naturforsch. Gesell. in Zürich*, 11, Heft III; *Bull. de l'Acad. de St. Petersburg*, 14, 517; *Ann. der Phys.*, 1872, 144, 280.

at 8° was placed in the cylinder surrounding the rubber; and the note given by the gut was observed. The water was then replaced by water at 50°; and it was found that the pitch of the note had increased by 12.8 per cent. With a stronger initial tension on the thread, the increase due to raising the temperature was greater, viz. 20.8 per cent.

2. A rubber cord was fastened between two blocks placed on a board; and it was found that the pitch of the note given by the cord was raised by immersion in hot water; the rise being greater, the greater the original stretch.

It will be noted that in both these experiments the rubber is held at constant length. The experiments cannot be regarded as doing more than demonstrating the increase of tension which would follow as a result of the effort on the part of the stretched rubber to retract.

Subsequent discussion of the Joule Effect has in almost every case had reference to the suggestion of Schmulewitsch, that the elastic modulus of rubber in a state of tension is raised by increase of temperature. The question, as it relates to the Joule Effect, of the change produced in the elastic modulus of rubber by increase of temperature is, however, as will appear in what follows, a somewhat complicated question and one which it is difficult to attack in an unambiguous manner.

*Measurement of the modulus by determination of the velocity of propagation of a disturbance through rubber.*—Recognizing the difficulty of attacking the question by the ordinary methods of determining the elastic modulus, *i. e.* by measuring the elongations produced by given loads, Exner<sup>1</sup> sought to study the modulus by measuring the velocity of sound in rubber. A rubber cord was put in a state of tension, one of its ends being held by a thread. The tension was lifted suddenly by burning the thread; and, by means of a Hipp's chronoscope and a suitable arrangement of circuits and contacts, the very small period of time required for the wave of contraction to proceed to the other end of the cord was measured. The rate of propagation of a disturbance in it gives the velocity of sound in the material in question. The chronoscope had previously been employed by Stefan<sup>2</sup> for determining the velocity of sound in rubber.

<sup>1</sup> *Sitzungsber. Wien*, 1874, 69, 102; *Ann. der Phys.*, 1874, 153, 62.

<sup>2</sup> *Sitzungsber. Wien*, 1872, 65 (II Ab.), 419. Earlier (*ibid.*, 1868, 57 (II Ab.), 697) the same author had made some vibrational measurements of the velocity of sound in rubber.

The following table shows the results obtained by Exner, with a piece of black, vulcanized rubber, when it was placed under a tension which stretched it to about twice its original length (original length = 1 m.) and was subjected to a range of temperatures.

TABLE CLVII

Temperature (°)	0	12	15	33	40	50	60	74
Velocity of sound (m. per sec.)	54.0	47.6	47.0	37.5	33.5	30.7	30.2	29.0

A sample of red rubber gave similar results; although in this case the actual velocity at any given temperature was higher than in the case of the black rubber. It was concluded from these results that the velocity of sound in stretched rubber, and, hence, the modulus of elasticity of stretched rubber, is reduced by increase of temperature.

Bouasse<sup>1</sup> subjects Exner's technique to criticism. He points out that it does not give a satisfactory determination of the modulus of elasticity at a given tension. When the thread holding the rubber cord is burned, the rubber is no longer either under constant tension or of constant length. At the end of each experiment the tension has fallen to zero; and the results are difficult of interpretation. Bouasse points out that the differences in the modulus as determined, in rubber under different conditions, by Exner's technique are much smaller than would be expected. The following table shows the change in the velocity of sound found by Exner in a rubber cord at atmospheric temperature with changes in the elongation. E shows the modulus of elasticity calculated from the formula  $E = kv^2$ , taking  $E = 1$  for  $\Lambda = 2$  (*i. e.* for a length of 200 per cent.).

TABLE CLVIII

	2	3	4	5
$v$ (metres)	47.2	56.2	62.9	65.9
$E$	1	1.41	1.77	1.95

The rate of increase of  $E$  with increasing elongation is, Bouasse believes, much smaller than would be expected. Thus Villari, calculating  $E$  after the same definition—although working on

<sup>1</sup> *Loc. cit.*, pp. 186-8.

other, and probably less extensible, samples of rubber—found  $E$  to increase in one case from 1 to 13, and in another case from 1 to 34 over the same range of elongation.

It would seem that, with a more satisfactory method of generating an impulse in the piece of rubber under investigation—a method which did not involve changing the length or the tension of the rubber—the determination of the velocity of sound in rubber should provide an unexceptional and interesting method of investigating the modulus of elasticity of rubber under various defined conditions of length, tension and temperature. It should be borne in mind, however, that the method gives only the adiabatic modulus ( $S$ ) and not the isothermal modulus ( $E$ ). And that it is the latter which is in question in the Joule Effect. The former modulus is related to the latter as  $S = C_p/C_v \cdot E$ ; but we do not know whether the ratio of the specific heats may not change with the tension and the temperature.

A second series of experiments by Exner is not open to the objection that may be raised against the series already described. In this second series the rubber was in the form of a massive rod, of "fine, grey, vulcanized rubber," 3 cm. square cross-section, and 1.6 m. long. The rubber was not under tension. A longitudinal impulse was generated in it, by striking one of the end surfaces with the finger. (It was shown experimentally that the velocity of propagation was not influenced by differences in the strength of the impulse.) The results obtained with this rod were as follows<sup>1</sup>:—

TABLE CLIX

Temperature (°)	0	10	22	45
Velocity of sound (m. per sec.)	43.2	40.8	37.4	32.3

*Influence of temperature on the modulus under no-load.*—The results shown in the above table lead to the conclusion that the modulus of elasticity of rubber *under no-load* diminishes with increase of temperature. And this conclusion may be regarded as confirmed by the experiments of Russner.<sup>2</sup> The experiments in question on the influence of temperature on the modulus of

<sup>1</sup> It may fairly be remarked, in view of Bouasse's criticism of the first series of experiments, that the range of variation of the velocity with temperature here shown by rubber under no-tension is not larger than but similar to that found by Exner in the experiments in which the rubber was under tension.

<sup>2</sup> *Repertorium*, 1882, 18, 206; *Ann. der Phys.*, 1891, 43, 533.



elasticity were made by the ordinary method of longitudinal loading accompanied by measurements of the elongation. In each case the rubber was first subjected to a given temperature while under no-load; and readings of stretch under increasing loads were then made, the temperature remaining constant throughout. The modulus was found to be lower at higher temperatures than at lower ones. Thus  $E$  for a sample dealt with in Russner's first paper changed with change in the temperature in the following way:—

TABLE CLX

Temperature (°) .	16	19	39	56	69
$E$ (kg./mm. <sup>2</sup> ) .	666.2	614.5	430.2	413.0	313.0

These figures refer to a maximal load of 150 g. on an original cross sectional area of 37 mm.<sup>2</sup> The data given by Russner refer entirely to very small loads; the maximal elongation recorded at the highest temperature employed being in no case much more than 10 per cent. The extent to which the modulus fell appeared to vary considerably in different samples of rubber.<sup>1</sup>

*Influence of temperature on the modulus as determined by torsional experiments.*—Graetz<sup>2</sup> attacked the question of the influence of temperature on the elastic modulus of stretched rubber by determinations of the rigidity or torsion modulus from the period of torsional oscillation. The relation between the torsion modulus ( $F$ ) and the stretch modulus or modulus of elasticity ( $E$ ) being taken, according to elastic theory, as  $F =$

$\frac{E}{2(1 + \sigma)}$ ; then, assuming  $\sigma$  to be substantially constant, the variation of  $F$  with temperature should give a measure of the variation of  $E$  with temperature. The period of oscillation was determined from eight to twenty oscillations. In the case of all the samples examined—two of red, two of grey and two of black rubber—increase of temperature produced a reduction in the oscillation period; or, rather (the measurements appear to

<sup>1</sup> The diminution of the modulus for the samples dealt with in Russner's second paper was, except for a sample of raw rubber, very much less marked than the diminution shown by the figures for the samples, one of which is quoted in Table CLX, in his first paper. The samples in question were a black rubber of specific gravity 0.947, a grey rubber of specific gravity 1.244, and black rubber tubes of specific gravities 0.943 and 0.930. In the case of the last two samples, there was no diminution at all.

<sup>2</sup> *Ann. der Phys.*, 1886, 28, 354.

have been made at successively lower temperatures), fall of temperature increased the period of oscillation. Thus in the case of a typical sample (black rubber) the oscillation period increased from 33.838 s. to 35.357 s. as the temperature fell from 52.1° to 20°. The load on the rubber in this case was 97.74 gms./cm.<sup>2</sup>; the elongation being given as 75.9 per cent.<sup>1</sup>

The increase in the period of oscillation with decrease in temperature being taken as indicating a corresponding decrease in the torsion modulus, Graetz concluded from his results that the isothermal elastic modulus of rubber under a constant load increases, as Schmulewitsch had supposed, with increase of temperature.

Russner<sup>2</sup> and Bouasse<sup>3</sup> have severely criticized Graetz's treatment: the former partly on the ground that the theory of elasticity does not, as Graetz assumed, apply; the latter on the ground that the torsion modulus is not suitable for determining a matter, such as the Joule Effect, in which only the elasticity in the longitudinal direction is in question. The torsion modulus is calculated from the formula—

$$F = \frac{2\pi}{8} \cdot \frac{kl}{t^2 r^4},$$

where  $l$  = the length;  $r$  = the radius;  $k$  = the moment of inertia of the weight, which effects the torsion, referred to the extension axis;  $t$  = the time of oscillation. Now, as the temperature fell in Graetz's experiments, the length of the rubber increased and the volume of it decreased; the new length being  $l(l + \alpha t)$  and the new radius  $r(l - \beta t)$ , where  $\alpha$  and  $\beta$  are the coefficients of expansion in the longitudinal and in the transverse directions respectively. Thus the torsion modulus at the lower temperature is—

$$F_1 = \frac{2\pi k}{g} \cdot \frac{l(l + \alpha t)}{t_1^2 r^4 (l - \beta t)^4}.$$

Now,  $\beta$  has a larger value for stretched than for unstretched rubber (*vide* p. 470); hence, it is readily possible that, despite an increase in the time of oscillation (*i. e.*  $t_1 > t$ ), the torsion modulus may be greater at the lower temperature than at the higher one (*i. e.*  $F_1 > F$ ).

In stretched rubber the elastic properties are different in the

<sup>1</sup> The linear expansion of the thread in falling from 52.1° to 20° was 9 per cent. of its length at the higher temperature.

<sup>2</sup> *Ann. der Phys.*, 1891, 43, 533.

<sup>3</sup> *Loc. cit.*, pp. 198–9.

longitudinal and in the transverse directions. The torsion modulus gives only a mean value for the elastic properties of stretched rubber, and therefore has not direct relation to the contraction in the longitudinal direction, which is characteristic of the Joule Effect.

*Observations of Lundal on the influence of temperature on the modulus.*—Another observer who has concluded that the modulus of elasticity is increased with rise of temperature is Lundal.<sup>1</sup> The method of observation employed was to subject the rubber, while under a constant, permanent load, to a series of increasing temperatures, and to determine at each temperature the elongation produced by small extra loads. It was found that the elongation produced per gram of extra load diminished as the temperature was increased; and it was concluded that the modulus of elasticity increased with increase of temperature. (The increase was approximately 10 per cent. over the range 3°–60°.) Figures obtained in Lundal's experiments for the linear expansion or contraction under different loads and at different temperatures have already been given in Table CLVI. It will be seen that in the case of two of the three loads in question a point of inversion occurs within the range of temperatures in question; increase of temperature from one step to the next first producing a contraction and then an elongation. Thus it would appear that the points on the stress-strain curve at which the observations were made is a rather unfortunate one. The investigation does not give evidence of a sufficient appreciation of the complexity of the question and of the necessity for circumspection in attacking it.<sup>2</sup> And the data, as they stand, do not seem acceptable as conclusive in favour of the view that the modulus of elasticity increases with increase of temperature.

The somewhat confused character of the discussion which has been carried on round the Joule Effect has perhaps been due largely to the failure of most of the protagonists to appreciate, or at all events to give sufficient prominence to the distinction, which, it would appear, must be kept in mind in regard to the

<sup>1</sup> *Diss., Upsala, 1897; Ann. der Phys., 1898, 66, 741.*

<sup>2</sup> It is open to question as to how successfully allowance was made for elastic after-effect. And, further, the author states that no corrections were introduced into the values for the elastic modulus on account of thermal dilatation of the rubber, and adds the significant remark (p. 754), "it is therefore, strictly speaking, uncertain whether the elastic modulus increases or decreases when the temperature rises."

variation of the modulus with temperature, between the modulus of elasticity under different conditions, namely :—

$$\begin{array}{l} \left\{ \begin{array}{l} \text{isothermal,} \\ \text{adiabatic,} \end{array} \right. \quad \left\{ \begin{array}{l} \text{no-load,} \\ \text{constant load,} \\ \text{constant length.} \end{array} \right.$$

*Work of Bouasse on the influence of temperature on the modulus.*—

The most satisfactory investigation of the influence of temperature on the modulus of elasticity of rubber is the investigation of Bouasse,<sup>1</sup> who examined the change of the modulus with change of temperature both at constant length and under constant load, using a different method for determining the modulus under each of these two conditions. By these methods, which have already been described (pp. 229, 235),

E is obtained from the inclination,  $\frac{dP}{dL}$ , of very small cycles of extension and retraction repeated a large number of times.

Considering first the modulus at constant length: In all experiments the quantity  $\epsilon$ ,<sup>2</sup> which at a given elongation is proportional to the modulus of elasticity, diminished with rise of temperature and increased with fall of temperature. The experiments followed widely different courses; but it was invariably found that, whenever the temperature was raised,  $\epsilon$  fell, and whenever the temperature dropped,  $\epsilon$  increased.

In a number of interesting experiments Bouasse<sup>3</sup> shows that the modulus is not a fixed function of the elongation and the temperature, but is influenced to a very considerable extent by the course of any operations to which the rubber may have been previously subjected, and that the result of comparing  $\epsilon$  at two temperatures depends essentially on the manner in which the experiment is carried out. Examples of this may be seen in the results quoted below. The following experiment was conducted over three days. The rubber cord used had not been previously heated. It had, however, been extended to  $\Delta 5$ .  $L_0 = 18$  cm.;  $t_0 = 14^\circ$ ;  $t_1 = 48^\circ$  (approx.).  $\epsilon$  was determined at  $t_0$ ; the burners of the heating arrangement were then lit, and the temperature was raised to  $t_1$  as quickly as possible;  $\epsilon$  was determined at  $t_1$  thirty minutes after it had been determined at  $t_0$ ;

<sup>1</sup> *Loc. cit.*

<sup>2</sup>  $\epsilon$  is used by Bouasse to indicate the inclination of the small cycles at any point. It is expressed in arbitrary units. As pointed out earlier, when multiplied by  $L^2$ , it gives E.

<sup>3</sup> Cf. Bouasse and Carrière, *Ann. Fac. des Scs. Toulouse*, 5 (2), pp. 314-8.

the burners were then extinguished;  $\epsilon$  was determined at  $t_0$  thirty minutes later, and so on;  $\epsilon$  being determined successively at  $t_0$  and at  $t_1$  at intervals of thirty minutes. Measurements were made first at successively higher and then at successively lower elongations.

TABLE CLXI

Length (cm.).	$\epsilon$ at				
	$t_0$	$t_1$	$t_0$	$t_1$	$t_0$
25	415	381	412	382	400
35	266	253	268	254	260
50	233	225	230	—	—
65	258	245	252	—	—
80	401	327	363	—	—
90	650	460	545	460	537
80	324	292	324	—	—
65	250	230	238	—	—
50	227	216	222	—	—
35	278	255	269	—	—
25	420	392	—	—	—

It will be seen that the modulus is always reduced by heating and increases on cooling. When, as above, the change from one temperature to the next is repeated for a number of times, the change of the modulus with change of temperature is greatest on the occasion of the first change. The modulus tends to assume a final or "fixed" value much more quickly at a higher temperature than at a lower one. In illustration of this last point it may be mentioned that at the conclusion of the above series of observations the temperature was held at  $t_1$  for two hours; and the value of  $\epsilon$  at  $t_1$  was then found to be unchanged at 392.

The growth in the value of the modulus after the rubber has been subjected to heat may be illustrated by the following data. At the conclusion of the above series of observations the specimen was extended to 90 cm. and was heated at  $t_1$  for two hours:  $\epsilon$  now showed practical constancy at 344. The temperature was lowered to  $t_0$ , and  $\epsilon$  increased as follows:—

TABLE CLXII

Time elapsed since heating	10 min.	1 hr. 40 m.	2 days 16 hrs.
$\epsilon$	425	531	574

Experiments following other courses also showed how greatly the magnitude of the effect of increased temperature on the

modulus was influenced by the character of any preceding operations on the rubber and by the length of any periods of rest involved.

Considering the influence of temperature on the modulus at constant load: this was found to change sign twice, as the load was increased. Under no-load ( $\Lambda = 1$ ) increase of temperature reduced the modulus; as the load was increased, the effect of increased temperature on the modulus became positive for lengths between  $\Lambda = 1$  and  $\Lambda = 2$ ; passed through a maximum; became zero; and then, usually for a length between  $\Lambda = 2$  and  $\Lambda = 3$ , became negative; and thereafter increased rapidly in absolute value, without changing sign, up to the highest elongations at which experiments were feasible. The following shows the result of an experiment in which the rubber at each load was submitted successively to temperatures of  $15^\circ$  and  $49^\circ$ . The original length was 20 cms. The values of  $\epsilon$  are in arbitrary units. In  $\frac{d\epsilon}{\epsilon}$ , the denominator is the mean of the values at the lower and at the higher temperatures. The hot period—counting from the lighting of the heating arrangement—was twenty minutes; the cold period—counting from the extinction of the heating arrangement—was also twenty minutes:  $\epsilon$  was determined a few minutes before the conclusion of each period.

TABLE CLXIII

Load (g.).	Length in the cold.	Contraction (cm.) on heating.	$\epsilon$ in cold.	$\frac{d\epsilon}{\epsilon}$ .
0	$\Lambda = 1$	- 0.09	115	- 0.023
2 × 66	$\Lambda = 1.28$	+ 0.29	74	+ 0.008 <sup>1</sup>
3 × 66	$\Lambda = 1.45$	+ 0.75	59	+ 0.015
4 × 66	$\Lambda = 1.69$	+ 1.30	47	+ 0.036
5 × 66	$\Lambda = 1.90$	+ 2.23	39	+ 0.050
16 × 66	$\Lambda = 5.47$	+ 9.13	112	- 0.700

It will be seen that, excluding from consideration small elongations, up to  $\Lambda = 1.12$ , although linear contraction on heating is accompanied by a small increase in the modulus of elasticity as far as loads corresponding to  $\Lambda = 2$  or 3, yet beyond these loads linear contraction is accompanied by a decrease in the modulus.

<sup>1</sup> For a load of 66 g.,  $\Lambda = 1.12$ ,  $\frac{d\epsilon}{\epsilon}$  was very nearly zero.

It appears from the above observations of Bouasse that an increase of the modulus of elasticity with temperature cannot be regarded as the determining factor in the Joule Effect.

And if the question of the influence of temperature on the elastic modulus of rubber is left on one side, as, for the purpose of explaining the Joule Effect would seem, at least provisionally, permissible, and the Joule Effect is considered merely in regard to the dimensional changes of the rubber in different directions, brought about by increase of temperature, another point of view, from which the Effect may be regarded more satisfactorily, although perhaps not completely, would seem to be attainable. And the following remarks are therefore added on the thermal expansion of rubber.

#### THE THERMAL EXPANSION OF RUBBER

It is necessary to distinguish, not only between (a) the linear coefficient of expansion in the longitudinal direction, (b) the linear coefficient in the transverse direction, and (c) the cubical coefficient, but also between the coefficients (1) under no-load, (2) under constant load, and (3) at constant extension. The linear coefficient in the longitudinal direction (a) has already been considered. Under no-load and at small loads it is positive;<sup>1</sup> but under most loads it is negative (the Joule Effect). But, in the Joule Effect, though the rubber shows a negative coefficient of linear expansion, it shows a normal, positive cubical coefficient. The establishment of this fact : that, although stretched rubber shows longitudinal contraction on being heated, this is not indicative of an actual, cubical contraction, is important. The following is a review of the investigations that have been made on the cubical expansion of rubber :—

(a) *Coefficient of cubical expansion under no-load.*—Joule found 0.000526 as the coefficient for a sample of vulcanized rubber (specific gravity : 0.99) weighed in water 2.25° above and 2.25°

<sup>1</sup> A reference may be made here to Schwartz and Kemp's observation (*loc. cit.*) that, if the sample of rubber, the linear coefficient of expansion of which was examined, had recently been extended, the coefficient under no-load might appear at first as negative. This was due to the removal of set under the influence of heat. Thus a sample of rubber, containing 88 per cent. of (Para) gum, which had been stretched to twice its length for five minutes and then allowed three to four minutes' rest, showed, on raising the temperature, a decrease of length up to a temperature of 45° (decrease at this point : 0.9 per cent.) and had reached its original length only when the temperature had been raised to 58°.

below the maximal density. Lebedeff<sup>1</sup> for a sample of vulcanized rubber found 0.00067. Lundal<sup>2</sup> determined the coefficient for a sample of black rubber (specific gravity, 0.90166 at 17.4°; sulphur-content 2.5–3 per cent.) for six intervals of temperature covering the range 0°–60.7°. The values found rose from 0.000700 at 0–15.22° to 0.000855 at 56.0°–60.7° (Mean value : 0.000763). For a sample of grey, vulcanized rubber, he found the mean coefficient to be 0.000562. For a sample of raw rubber Russner<sup>3</sup> found a similar value. Determinations were made over the range 0°–75.1°; the mean values obtained being—at 10°, 0.000657; at 20°, 0.000665; at 30°, 0.000670.

The coefficient of cubical expansion of rubber is greater than that of almost any other solid body. The following procedure<sup>4</sup> can be used to demonstrate in a simple way the high magnitude of the coefficient : Take a piece of rubber of a density somewhat below that of boiling water—say, thread of specific gravity 0.98; throw the rubber into the water; it sinks; but in a very short time the heat has expanded it sufficiently to bring it up to the surface. Or,<sup>5</sup> take a piece of rubber which is lighter than cold water; stick pieces of iron wire into it to cause it to sink; heat the water. The rubber rises to the surface as the temperature of the water rises.

(b) *Coefficient of cubical expansion at constant length.*—The coefficient at constant length is conveniently examined by winding rubber, stretched to a given extent, on a frame. For the sample of rubber for which he had found the value 0.0067 for the coefficient under no-load, Lebedeff found at a constant elongation of 100 per cent. the value 0.0068. Russner<sup>6</sup> found the coefficient at constant extension to be identical with the coefficient under no-load. Lundal<sup>7</sup> also found such to be the case. For the sample of black rubber which gave 0.000763 for the mean value of the coefficient under no-load between 0° and 60.7° he found, under a constant elongation of 67 per cent., a mean value of 0.000761 between 14° and 50°. For the strip of grey, vulcanized rubber, which under no-load gave a mean coefficient between 15° and 50° of 0.000562, the coefficient at the

<sup>1</sup> *J. Russ. Phys. Chem. Soc.*, 1881, **13** (2), 246 (*Chem. Centralbl.*, 1882, 17).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Repertorium*, 1882, **18**, 159.

<sup>4</sup> Described by Thomas, *Les Mondes*, 1869, **19**, 575.

<sup>5</sup> Villari (*Ann. der Phys.*, 1871, **143**, 305) states that this modification provides a more satisfactory demonstration.

<sup>6</sup> *Repertorium*, 1882, **18**, 206.

<sup>7</sup> *Loc. cit.*



extension—probably 100 per cent. or more—produced by a load of 58.3 g./mm.<sup>2</sup> was 0.000560.

(c) *Coefficient of cubical expansion under constant load.*—The experimental arrangement employed by Russner<sup>1</sup> for the examination of the coefficient under a condition of constant load was as follows: The rubber was taken in the shape of a strong tube. A glass tube was firmly bound to each end of the rubber tube, the upper glass tube being bent so as to form a hook. The rubber, with its glass mountings was placed in a long, vertical glass tube; the lower mounting being sealed to the bottom of this tube. A wire was attached to the hook of the upper mounting, and passed through a narrow glass tube, sealed on to the end of the containing glass tube. The wire was attached to one end of a balance beam, so that the rubber could be stretched by loads put in the pan at the other end of the beam. The glass vessel containing the rubber was filled with water. Observations were made of the volume change, indicated by the position of the water in the narrow tube, when the temperature was raised to the boiling-point of water. Observations were made with elongations increasing up to 200 per cent. It was found that the increase in volume of the stretched rubber was the same as that of the unstretched.<sup>2</sup>

*Conclusion.*—As in the case of modulus of elasticity, so, in relation to the Joule Effect, in the case of the coefficient of cubical expansion, investigators have not always clearly distinguished between the value at constant length and the value at constant load. It seems sufficiently certain, however, from the data given above, that the coefficient of cubical thermal expansion is the same under both conditions and is identical with the coefficient under no-load. Hence, in the Joule Effect, the cross-section increases to an extent sufficient to bring about cubical expansion in spite of the linear contraction; that is to say: the coefficient of expansion of stretched rubber is different

<sup>1</sup> *Loc. cit.*

<sup>2</sup> It should perhaps be noted that the heating proceeded slowly, so that the linear contraction produced by increase of temperature was never very great. It may be remarked here that the influence of the rate of heating, and of the duration of heating on the change of strain in rubber under stress, has not been examined as closely as would seem to be desirable. In the description of most experiments on the Joule Effect, no information on these points is given. Yet Russner notes that the rate of heating influences the amount of contraction observed; the quicker the heating, the greater being the contraction.

in different directions, being, in general, negative in the longitudinal and positive in the transverse direction. Hence it is possible to regard the Joule Effect from the point of view suggested by Russner.<sup>1</sup> From this point of view stretched rubber is to be considered as presenting only an exaggerated case of the behaviour in regard to thermal expansion which is not infrequently presented by such typically anisotropic bodies as crystals. It is well known that the coefficient of expansion of crystals is different in different directions and can be—as; for example, is the case with calcspar or silver iodide—negative in the direction of one axis. Now, in stretched rubber we have a markedly anisotropic body; and its anisotropy may be regarded as displaying itself in the exhibition of different coefficients of expansion in different directions. The anisotropy of stretched rubber may also be seen, as remarked later, in (*a*) double refraction, (*b*) dichromatism, (*c*) electrification by mechanical deformation (analogy to piezo-electricity in crystals), (*d*) different values for Poisson's ratio in different directions.

The behaviour of muscle, with respect to the inter-relation of thermal and tensile effects, shows considerable analogy to the behaviour of rubber. The view which would regard the contraction of stretched rubber when heated as referable to its anisotropic character—contraction taking place along one axis and expansion along another—has considerable similarity to the view of muscular contraction which has been proposed by Engelmann.<sup>2</sup> It should, however, be mentioned that, more recently, views of muscular contraction have been developed, which would refer it to surface tension at the surface of the fibrillæ.<sup>3</sup> Surface tension possesses a negative temperature coefficient. No view corresponding to this last-mentioned one has been put forward in the case of rubber.

It must be said that the Joule Effect, and, generally, the inter-relation of thermal and mechanical behaviour in rubber demand fuller investigation.

No investigations have yet been made into the influence of the

<sup>1</sup> *Repertorium*, 1882, **18**, 206.

<sup>2</sup> "Ueber den Ursprung der Muskelkraft," 2. Aufl., Leipzig, 1893; "Kontraktilität und Doppelbrechung," *Sitzungsber.*, Berlin, 1906, 694.

<sup>3</sup> Bernstein, *Archiv (Pflüger's) f. Physiol.*, 1901, **85**, 271, 1908, **122**, 129; Macallum, *Ergeb. Physiol.*, 1911, **11**, 589, *J. Biol. Chem.*, 1913, **14**, 96. Cf., however, Berg (*Biochem. Bull.*, 1912, **2**, 101), who states that surface tension energy is insufficient to account for the lifting power of muscle.

character of the compound, and of the state of cure on the inter-related mechanical and thermal effects in rubber, or on the relation of these effects to rubber in technical use.

#### OPTICAL RELATIONS

*Double refraction.*—It has long been recognized<sup>1</sup> that isotropic bodies frequently become double refracting when mechanically deformed. Rubber is among the bodies which exhibit "accidental" double refraction when subjected to mechanical deformation. Accidental double refraction has been extensively studied in the case, particularly, of glass, but in the case of rubber the first observations (Bjerkén's) were made only in 1891.<sup>2</sup> The following table shows Bjerkén's results, on the change of the double refraction with change in the mechanical deformation, in the case of a sheet of rubber, 24.6 mm. broad, 47 mm. long and 0.25 mm. thick.  $n_o$  and  $n_e$  indicate respectively the refractive indices, relative to the D line, for the ordinary and the extraordinary rays. The left-hand half of the table shows the effect of loading up to the point at which the length of the specimen was 5.34 times its original length. The right-hand half shows the effect of unloading.

TABLE CLXIV  
*Double refraction produced by mechanical strain*  
 $L_0 = 47$  mm.

Increasing load.					Decreasing load.				
P (kg.).	L (mm.).	P (kg./mm. <sup>2</sup> ).	In- crease in length (per cent.).	( $n_o - n_e$ ) $\times 10^6$ .	P (kg.).	L (mm.).	P (kg./mm. <sup>2</sup> ).	In- crease in length (per cent.).	( $n_o - n_e$ ) $\times 10^6$ .
0	47	0	—	—	0.71	248	0.609	428	17.590
0.21	78	0.0567	66	1,390	0.61	243	0.513	417	17.240
0.31	115	0.123	145	2,530	0.51	238	0.420	406	17.060
0.41	157	0.223	234	4,670	0.41	231	0.328	391	16.470
0.51	205	0.362	336	8,190	0.31	211	0.226	349	12.870
0.61	227	0.479	383	13,000	0.21	92	0.0668	96	1,800
0.71	241	0.592	413	15,020	0.11	59	0.0225	25	560
0.81	251	0.7035	434	16,640	—	—	—	—	—

<sup>1</sup> Cf., e. g., Brewster, *Phil. Trans.*, 1815, 1816.

<sup>2</sup> *Ann. der Phys.*, 1891, 43, 808.

Stretched rubber is seen to exhibit negative double refraction, *i. e.* the index of refraction is greater for the ordinary ray than for the extraordinary ray.

Regarding the relation of accidental double refraction to the elastic modulus of the body in question: Bjerkén concludes, from his more extensive experiments on gelatine preparations of different degrees of stiffness, that, in general, the double refraction associated with a given stretch is greater, the greater the elastic modulus. The possible relation between accidental double refraction and the elastic constants in different samples of rubber has not been investigated. It is, however, of some interest to bring together, as is done in the following table, the figures (calculated from small increments of length) for Bjerkén's sample of rubber, his strongest and his weakest gelatine preparation and a sample of glass investigated by Wertheim—four materials with different moduli of elasticity.

TABLE CLXV

E = the elastic modulus (the stretch modulus) in kg./cm.<sup>2</sup>.  $\beta$  = the double refraction corresponding to a load of 1 gm./cm.<sup>2</sup>.  $\gamma = (n_o - n_e)$  for an increase of length of 1 per cent.

	E.	$\beta \times 10^6$ .	$\gamma \times 10^4$ .
Gelatine (Sample 1) .	0.125	1.37	0.0172
" ( " 2) .	3.6	0.17	0.0615
Rubber . . . .	10.0	0.25	0.25
Crown glass . . .	70,000	0.000186	13.0

Bjerkén's measurements did not indicate that the double refraction bore any simple relation to either the elongation or the load. More recently Rossi<sup>1</sup> has investigated the relation of accidental double refraction in rubber to the deformation and the stress. He worked with thin sheets of rubber, of 0.17 to 0.7 mm. in thickness, and consisting of "pure Para rubber." He measured the double refraction by means of a Babinet-Biot compensator. He found that the relation between the double refraction and the percentage elongation was not constant. It was approximately constant only so long as the elongation produced was approximately proportional to the load; and, even so, was approximately constant only during the loading

<sup>1</sup> *Rend. di Napoli*, 1910, **16** (3), 125, 142; *Cimento*, 1910, **20** (5), 226, 268; *Ibid.*, 1911, **2** (6), 151 (*Beibl. Phys.*, **35**, 206, 364, **36**, 67; *Fortschr. Phys.*, 1910, **11**, 394).

period. During the unloading period the ratio diminished as the load decreased. It was concluded that the ratio of the double refraction to the load per unit area showed much greater constancy than the ratio to the elongation. The behaviour of vulcanized and of non-vulcanized rubber was found to be practically identical.

Rossi notes an interesting parallelism between the influence of after-effect on the deformation and its influence on the double refraction. On holding the rubber for a considerable period of time at a constant extension, it undergoes both mechanical and optical relaxation; and the diminution of tension and of double refraction is found to occur in the same ratio.

*Absorption. Dichromatism.*—A phenomenon which frequently accompanies double refraction is dichromatism. But, although the production of double refraction by mechanical deformation was well known, no case of dichromatism produced by strain was known until Kundt,<sup>1</sup> in 1874, observed that stretched rubber (and also gutta-percha) exhibited very strong double refraction. He called dichromatism so produced "temporary dichromatism," as it disappeared with the removal of the stress. He made qualitative observations only. He found the ray the vibrations of which fell in the direction of the pull to be more strongly absorbed than the other ray.

TABLE CLXVI

$\lambda$ .	$i'_z$ .	$i''_z$ .	$-\log i'_z$ .	$-\log i''_z$ .	$Q$ .
6572	0.607	0.310	0.217	0.509	2.345
6201	0.553	0.271	0.257	0.567	2.206
5889 { the D }	0.525	0.249	0.280	0.604	2.157
5630 { line }	0.484	0.214	0.315	0.670	2.128
5407	0.448	0.185	0.349	0.733	2.100
5212	0.414	0.167	0.383	0.777	2.030

Pulfrich<sup>2</sup> made some quantitative measurements on absorption by stretched rubber. Moderately clear rubber was drawn out and cemented between two plates. (The extent to which the rubber was drawn out is not stated.) The absorption of light of various wave lengths was then measured: the results obtained are shown in the above table. The incident light being taken as 1,  $i'_z$  and  $i''_z$  represent the residual light after passage

<sup>1</sup> *Ann. der Phys.*, 1874, 155, 125.

<sup>2</sup> *Ibid.*, 1881, 14, 193.

through the rubber; the negative logarithms of these quantities give the absorption coefficients; and the ratio  $-\log i_z'' / -\log i_z'$  gives the Absorption Ratio (Q).

It will be observed that in both spectra the absorption increases towards the blue, *i.e.* both  $i_z'$  and  $i_z''$  diminish. The ratio of the two absorptions does not, however, remain constant, but diminishes.

It may be mentioned that the general indication of some preliminary experiments on the light absorption of a thin sheet of calendered raw rubber, made by the use of a Hilger constant deviation spectroscope and a photo-electric cell, which have recently been communicated,<sup>1</sup> is also to show an increased absorption towards the blue end of the spectrum.

The absorption by rubber of infra-red rays was determined by Rubens,<sup>2</sup> who obtained the following results, which show the absorption of such rays by rubber to be almost or entirely complete.

Wave length.	Incident rays transmitted by rubber 1 mm. thick.				
24 $\mu$	.	.	.	.	0 per cent.
52 $\mu$	.	.	.	.	3 " "
61 $\mu$	.	.	.	.	6 " "

Now that it has become possible to obtain from the plantations very pale rubber, the investigation of the optical properties of rubber would seem to be greatly facilitated; and a more extended investigation of the relation between mechanical and optical behaviour in the case of rubber would probably yield interesting results.

#### ELECTRICAL RELATIONS

*Electrification produced by mechanical strain.*—That rubber becomes electrified on being stretched can readily be demonstrated by stretching a strip of rubber between the hands and then bringing it near a charged electroscope. Ashton<sup>3</sup> describes the following experiment. A sheet of "pure Para rubber [? calendered raw rubber] which had been rolled out to a thickness of 0.012 mils" was placed between two brass plates, which were connected with a quadrant electrometer, the upper and smaller plate being 6 ins. in diameter and 0.25 in. in thickness. A 2-lb. weight was dropped on to the top plate from a height of 3 ins.

<sup>1</sup> Observations of R. C. Dearle and E. K. I. Pratt communicated to the Roy. Soc., Canada, May 1919, by Dr. E. F. Burton.

<sup>2</sup> 1900.

<sup>3</sup> *Phil. Mag.*, 1901, 2 (6), 233.

The spot of the electrometer moved very quickly off the scale to the right, but immediately returned and settled down to a fairly steady deflection to the left. It appeared that the electrometer received two impulses—one due to the compression of the rubber, and a second, following shortly on the first, due to the recovery from compression. The effect of stretching the rubber was then observed. A fresh sheet, 0.22 in. thick, was placed between the brass plates; the edges were grasped gently in the hands, and the sheet was extended by about 30 per cent. This caused the electrometer spot to fly off the scale to the right, showing a difference of potential of at least 7 volts established between the plates. The top plate was negative. The condenser and electrometer were then discharged for an instant, and the sheet was allowed to return to its original dimensions. The result was that the electrometer spot flew off the scale to the left, the E.M.F. being more than 10 volts. The top plate was positive. The same phenomena were observed when the sheet of rubber was reversed, viz. extension made the top plate negative; contraction made it positive.

Ercolini<sup>1</sup> and Corbino<sup>2</sup> also noticed the electrification of rubber by mechanical strain. The former mentions specifically that it takes place with vulcanized rubber.

*Rubber as a dielectric.* N. Schiller<sup>3</sup> found the following figures for the dielectric constants of samples of rubber.

	Frequency.	D.E.	Frequency.	D.E.
(a) " Pure rubber (brown) "	0.0000663 sec.	2.12	$\frac{1}{40} - \frac{1}{60}$ sec.	2.34
(b) Vulcanized rubber (grey)	0.0000706 „	2.69	$\frac{1}{40} - \frac{1}{60}$ „	2.94

According to the electro-magnetic theory of light, the square of the index of refraction of a medium is equal to its dielectric constant. Schiller measured the refractive index of the former of the above two samples and found it to be 1.50; a figure which, when squared, gives a value (2.25) for the dielectric constant of the rubber in question conforming very fairly with the value found experimentally.

<sup>1</sup> *Cimento*, 1901, 2 (5), 297; *Riv. sci. industr., Firenze*, 1902, 34, 49 (*Beibl. Phys.*, 1903, 69; *Fortschr. Phys.*, 1901, 11, 401).

<sup>2</sup> *Cimento*, 1902, 3 (5), 85.

<sup>3</sup> *Ann. der Phys.*, 1874, 152, 335.

Gordon,<sup>1</sup> using a frequency of 0.000083, found the following values:—

	Specific inductive capacity.
"Plain black india-rubber" ( <i>i. e.</i> raw rubber) .	2.220
Vulcanized india-rubber .	2.497

*Mechanical deformation of rubber in an electric field. Electrostriction.*—The mechanical deformation of dielectrics under the influence of an electric field has been the subject of much discussion among physicists since the time, in the early part of the nineteenth century, when it was remarked that a Leyden jar increased its volume on being charged. But the experimental work on this general subject has been mostly confined to glass, ebonite, various liquids, etc., as dielectrics, and has dealt with soft rubber only to a comparatively limited extent. As, however, Young's modulus enters into the mathematical expression of such deformation, it is to be expected that a dielectric so readily deformable as rubber will show, under the influence of an electric field, deformations of a much greater order of magnitude than those shown by, say, glass. And that in fact it does so would appear from the results of Korteweg and Julius.<sup>2</sup> In the experiments of these investigators, as in most subsequent experiments on the same subject, the rubber was in the form of a tube, placed in water and filled inside with water, *i. e.*, substantially, a Leyden jar with water armatures. The change in volume was measured by observing the change in level in a capillary tube attached to the inside of the tube.

The experiments were made with "white, vulcanized rubber." It was concluded that the change of volume was proportional to the sparking distance, and inversely proportional to the square of the thickness of the wall. The change of volume was found to be very much greater than that observed for glass condensers under the same potential gradient; and, in fact, to be in the inverse ratio of Young's modulus for the two materials. The

<sup>1</sup> *Phil. Trans.*, 1879, **170**, 417.

<sup>2</sup> *Sitzungsber. Wien*, 1881, **83** (II Ab.), 29; *Ann. der Phys.*, 1881, **12**, 647.



mechanical deformation is given by an expression which in its simplest form,<sup>1</sup> as developed by Maxwell, is—

$$\frac{\Delta v}{v} = \frac{3kV^2}{8\pi E d^2},$$

where  $\frac{\Delta v}{v}$  indicates the change of volume referred to the original volume;  $k$  is the dielectric constant;  $V$  the potential difference between the armatures;  $E$  Young's modulus and  $d$  the thickness of the dielectric. Thus, comparing glass and rubber, the deformation  $\left(\frac{\Delta v}{v}\right)$  multiplied by  $d^2$  should for equal differences of potential, approximately, be inversely proportional to Young's

TABLE CLXVII

Volume change given in millionth parts of the original volume. Sparking distance: 4 mms.

		Thick- ness of walls. (mms.)	$\frac{\Delta v}{v} \cdot 10^6$	$\frac{\Delta v}{v} \cdot d^2 \cdot 10^8$	$\frac{\Delta v}{v} \cdot d^2 \cdot 10^8$ 40,000.
Flint glass ther- mometer bulb	No. 22 (Quincke, p. 190)	0.286	11.7	0.96	—
	" 21 . . . . .	0.319	6.651	0.68	—
	" 17 . . . . .	0.346	5.889	0.70	—
	" 61 . . . . .	0.407	2.950	0.49	—
	" 60 . . . . .	0.591	0.744	0.26	—
	" 35 (Quincke, p. 329)	0.206	8.700	0.37	—
Rubber tube, 1.06 m. long		2.25	2,290	11,600	0.29
" " 0.75 m. "		2.25	2,750	13,900	0.35
" " 1.08 m. "		0.95	15,400	13,900	0.35

modulus for the two materials. For the rubber tubes employed by them, Korteweg and Julius determined, by direct tractional measurements, with elongations up to about 9 per cent., the value of Young's modulus as 0.080 kg./mm.<sup>2</sup>. For samples of flint glass, the electrical expansion of which was determined by Quincke,<sup>2</sup> the modulus was 3280 and 3044. Thus the modulus for flint glass is about 40,000 times that for the rubber tubes in question. In the following table Korteweg and Julius' results for the electrical expansion of rubber, and Quincke's for the electrical expansion of flint glass, are given. It is seen that

<sup>1</sup> For more recent modifications of this formula, see papers by Sacerdote in the *Journal de Physique* (1901) and elsewhere.

<sup>2</sup> *Ann. der Phys.*, 1880, **10**, 197, 514.

$\frac{\Delta v}{v} \cdot d^2$ ) for rubber, when divided by 40,000, gives quantities noticeably similar to the values of  $(\frac{\Delta v}{v} \cdot d^2)$  for glass.

More recently the mechanical deformation of rubber under the action of an electric field has been studied by Ercolini, Cantone and Bouchet. It is not proposed to enter here at any length into the more controversial aspects of the question of electrostriction. More,<sup>1</sup> as a result of experiments with glass and ebonite, denies the existence of electrostriction. He would apparently confine the term electrostriction strictly to the production of elongation in dielectrics as a result of the *direct action* of the electric flux in a non-conductor; and he would ascribe the results obtained by earlier experimenters to the pressure deriving from the electrostatic attraction of the armatures and to the heating effect. Shearer<sup>2</sup> also denies the existence of electrostriction, and ascribes the results obtained chiefly to the heating effect. Neither of the investigators just mentioned worked with soft rubber; and investigations with this material would seem to agree in finding an electrostrictive effect.

Working with rubber tubes, Ercolini, in order to meet the objection that their lengthening in an electric field might depend, not on electrostriction, but on warming, used *stretched* rubber, in the case of which the effect of warming would be to produce contraction and not elongation. The rubber was stretched by amounts varying from 20 to 50 per cent.; and still an elongation was observed. That the mechanical deformation of rubber in an electric field cannot be attributed entirely to the electrostatic pressure of the armatures and the heating effect, is further rendered probable by measurements made by Bouchet.<sup>3</sup> This author, also working with an apparatus similar to that indicated above, and consisting of a rubber tube and water surfaces—the potential difference between which ranged from 550 to 2520 volts—observed that the deformation, as indicated by the fall in level in the capillary tube, required two minutes to complete itself, whereas the limit of deformation with mechanical forces of the same order was reached in twenty seconds. He observed,

<sup>1</sup> *Phil. Mag.*, 1900, **50** (5), 198; 1903, **6** (6), 1; 1905, **16** (6), 676. See, however, for a suggested explanation of More's negative result, E. C. Kembley, *Phys. Rev.*, 1916, **7**, 614. For other work relative to controversy on electrostriction, see papers by Sacerdote, Cantone, Adams and Heaps, Wüllner and Wien.

<sup>2</sup> *Phys. Rev.*, 1902, **14**, 89.

<sup>3</sup> *C. R.*, 1915, **160**, 240.

further, by direct measurements, that the heating due to the Joule Effect was negligible. For a potential difference of 2500 volts and a duration of charge of two minutes, it was only  $3.4 \times 10^{-4}$  degrees. Cantone, using a different experimental method, also maintains the reality of electrostriction in soft rubber.

TABLE CLXVIII

Diameter of the discs = 15 cms. The vulcanized rubber was non-mineralized.

$k$ .	$\frac{1}{E}$	$e$ (cm.).	$V$ (electro- static units).	$\Delta e$ (cms.).	$\Delta e'$ (calcd. for the electrostatic pressure).	$\Delta e - \Delta e'$ .
No. 1. PARA RUBBER.						
4	$3.1 \times 10^{-8}$	0.65	16.4	$-3.0 \times 10^{-6}$	$-2.05 \times 10^{-6}$	$-0.95 \times 10^{-6}$
	"	"	27.6	-7.5	-5.8	-1.7
	"	"	38.3	-15.0	-11.0	-4.0
No. 2. PARA RUBBER.						
4	$2.8 \times 10^{-8}$	0.35	16.4	$-4.5 \times 10^{-6}$	$-3.35 \times 10^{-6}$	$-1.15 \times 10^{-6}$
	"	"	27.6	-10.5	-8.7	-1.8
	"	"	38.3	-22.5	-18.7	-3.8
4?	$4.10 \times 10^{-8}$	0.30	16.4	$-5.1 \times 10^{-6}$	$-5.4 \times 10^{-6}$	$0.32 \times 10^{-6}$
	"	"	27.6	-19.5	-16.25	-3.24?
	"	"	38.3	-33.3	-31.2	-1.8

In later experiments, with rubber in the form of discs, Bouchet<sup>1</sup> finds that, under the action of an electrostatic field, vulcanized rubber contracts in the direction of the lines of force. The magnitude of the contraction observed is shown in the above table. In this table the extent of the contraction due to the electrostatic pressure of the armatures, calculated from the formula  $\Delta e = \frac{1}{E} \cdot \frac{kV^2}{8\pi e}$  ( $e$  = thickness,  $k$  = apparent dielectric constant,  $V$  = potential difference), is also given. The difference between this quantity and the observed diminution of thickness is attributed to the direct action of the field and is, in the case of the vulcanized rubber, almost proportional to the square of the difference of potential. In the case of the raw rubber, the

<sup>1</sup> C. R., 1916, 163, 479.

action proper of the field is not so apparent as in the case of the vulcanized material. The raw rubber sample is stated to have shown an enormous residual deformation.

*Change of dielectric constant on stretching.*—Corbino and Cannizzo<sup>1</sup> found the dielectric constant of rubber to diminish on stretching. They found the relative diminution,  $\frac{k - k'}{k}$ , to be, within the loads used, directly proportional to the load, so that  $k' = k(l - Al)$ , where  $A$  is a constant and  $l$  is the elongation of the rubber plate. Ercolini<sup>2</sup> attributes the finding of a negative change of the dielectric constant with stretched rubber by Corbino and Cannizzo to failure to take account of the electrification of rubber on being stretched; and he concludes that the change is a positive one. Lampa<sup>3</sup> reported a change in the dielectric constant of a rubber plate, on stretching, agreeing with the expectations of his theory of anisotropic electrics, from 2.263 to 2.727.

L. Schiller<sup>4</sup> has made a careful study of the change of the dielectric constant of rubber on stretching it at right angles to the lines of force, with the object of throwing light, if possible, on the intimate physical structure of stretched rubber. He urges that an investigation in which long waves are used is more likely to give an insight into the orientation of the molecules on tension than is an optical investigation, because into a consideration of the results of the latter the vibrations of the molecules themselves would enter as a complicating factor. He finds a negative change of the dielectric constant with tension; and, from a consideration of his results in the light of Wiener's theory on the dielectric constants of mixed bodies,<sup>5</sup> he comes to the conclusion that in the deformation of rubber we have to do, not merely with the anisotropic arrangement of molecules which are themselves isotropic, but, rather, with the orientation of molecules which were originally or which become themselves actually stretched. Schiller's numerical results were, in summary, as follows:—

Amount of extension.	Change in the dielectric constant.
(a) From 6.5 to 36.8 per cent.	From 3.655 to 3.525.
(b) From 7.8 to 43.9 per cent.	From 3.675 to 3.485.

<sup>1</sup> *Rend. Linc.*, 1898, **7** (5), 286 (*Fortschr. Phys.*, 1898, II, 427).

<sup>2</sup> *Cimento*, 1902, **3** (5), 85. <sup>3</sup> *Sitzungsber. Wien*, 1902, **111** (II Ab.), 984.

<sup>4</sup> *Ann. der Phys.*, 1911, **35** (4), 931.

<sup>5</sup> R. O. Wiener, *Phys. Zeit.*, 1904, **5**, 332; *Leipziger Ber.*, 1909, **61**, 113; 1910, **62**, 256.

*Mutual relations of mechanical and electrical strains in rubber.*—From what has been said, it appears that, on the one hand, the mechanical deformation of rubber leads to its electrification, and, on the other hand, that subjection to the action of an electrical field leads to the mechanical deformation of rubber. The question of the reciprocal action of mechanical and electrical forces in rubber has hitherto received no attention in regard to the technical application of rubber; but it is not impossible that it may have interesting technical bearings.

*Modulus of elasticity of calendered rubber in different directions.*—Mention may be made at this point of a curious phenomenon, to which the author's attention has been called by W. B. Wiegand. It is possible to demonstrate the presence in calendered sheet of a state of strain, which can perhaps be conveniently referred to as a "grain." Wiegand demonstrates the condition in question neatly in the following manner: On a piece of very thin calendered sheet, which has been prepared from pale crêpe, there is traced a circle of, say, 10 cms. diameter; and the direction in which the sheet passed through the calender is indicated by an arrow. The sheet is then either warmed for a short time up to 250° F., or, better, is immersed for a short time in a rubber solvent—say, carbon tetrachloride. This treatment enables the rubber to come out of its state of strain; and the circle is found to have become an ellipse, with its major axis at right angles to the arrow.

A few quantitative measurements relative to this phenomenon have been communicated.<sup>1</sup> Calendered sheets of pale crêpe,  $\frac{1}{16}$ th in. thick, were swollen in a mixture of forty parts of ether and five parts of alcohol. The swelling attained a maximum in five hours, and was as follows:—

In the direction of the calender	. . . . .	25.0 per cent.
At right angles to the direction of the calender	: . . . .	38.7 " "
" " " " " plane of the calender	. . . . .	30.0 " "

Young's modulus in the three directions was determined. Cubes of about 2 cms. side were cut from thick calendered sheet, and Young's modulus was measured for small strains—up to, say, 50 per cent. elongation. The results were as follows:—

		Young's modulus of calendered sheet.
In the direction of the calender	. . . . .	2345 gms./cm. <sup>2</sup>
At right angles to the calender direction	: . . . .	638.3 "
" " " " " plane of the calender	. . . . .	718.6 "

<sup>1</sup> In a paper by H. A. Braendle, communicated by Prof. E. F. Burton to the Roy. Soc. Canada, May 1919.

It is not inconceivable that the interaction of mechanical and electrical forces may be concerned in the production of the state of strain in calendered sheet which such results indicate. It is well recognized that very large amounts of static electricity may be generated in the neighbourhood of the mills in rubber factories.

## CHAPTER XXI

### POISSON'S RATIO

THE question of the relation between the change of dimensions in one direction, and the change, in the opposite sense, in the direction at right angles, when rubber is subjected to deformation, *i. e.* the question of the relation expressed by what is generally termed Poisson's Ratio, has been the subject of a good deal of discussion. The question of the change of volume of rubber on deformation is essentially an aspect of the same topic. The question of the magnitude of Poisson's ratio has an especial interest, because of the circumstance that rubber, at all events when non-mineralized, presents us with the case of a solid body which readily changes its form, but, apparently, changes its volume hardly at all. For metals, Poisson's ratio—generally represented in English and French literature by  $\sigma$ —is usually considerably smaller than 0.5. For a body which does not change its volume when deformed,  $\sigma = 0.5$ .

Whilst the result of the fairly considerable number of investigations which have been made into the magnitude of Poisson's ratio for rubber is to show that nearly all agree in finding it to approximate to 0.5, they indicate a *small* increase in the volume of rubber on extension. A recent investigation (by Schippel, *vide* p. 498) indicates that the value of Poisson's ratio for rubber is very considerably influenced by the amount and character of any compounding ingredients which it may contain.

A discussion in some detail of the various investigations which have been made into Poisson's ratio for rubber is desirable for several reasons. In the first place, the investigations afford an instructive example of the necessity for caution in applying to a material so deformable as rubber definitions of elastic constants which have been developed in connection with much less deformable materials, such as metals. In the second place, a review of the experimental methods which have been employed in connection with the question is of interest. Further, the recent development of the question, namely, the demonstration, in the

work of Schiller, of different values of  $\sigma$  in different directions, is of significance in connection with the anisotropy produced in rubber by deformation. And, finally, a new and important practical aspect of the question is suggested by Schippel's work on the influence of the composition of the rubber compound on the increase of volume produced by stretching.

*Methods of determining Poisson's ratio.*—The methods by which Poisson's ratio has been measured may be divided, in the first instance, into (a) determinations by cubical measurements, (b) determinations by superficial (two-dimensional) measurements. The former of these methods comprises (a') measurements of specific gravities by hydrostatic weighing, (a'') direct measurements of volume change by observing the change of level of water when rubber immersed in it is deformed. In the first method (a) the change of volume associated with a given change of one dimension—usually, the length—is measured. In the second method (b) the simultaneous change of dimensions longitudinally and materially is measured on a plane surface.

*Wertheim's measurements.*—The first recorded measurements of Poisson's ratio for rubber are due to Wertheim.<sup>1</sup> They were made on rubber cords of circular cross section.<sup>2</sup> The cords were stretched in a horizontal position. The change in length, as measured between two gauge marks, lying, in order to avoid curvature of the sides, clear of the grips; and the change of diameter was observed. Direct measurement was used for observing the diameter. Owing to the softness of rubber, the direct measurement of the thickness of rubber samples does not permit of great accuracy; and, in fact, all subsequent investigators of Poisson's ratio for rubber have employed methods which do not involve the direct measurement of the thickness.

Some of Wertheim's results are shown in the first five columns of the following table. (Reference will be made later to the sixth row.)

Wertheim concluded that the ratio of transverse contraction to longitudinal extension was  $\frac{1}{3}$ <sup>3</sup> for comparatively small extensions, and that with greater extensions it fell below  $\frac{1}{4}$ .

<sup>1</sup> *Ann. de Phys. Chim.*, 1848, 23, 54-7.

<sup>2</sup> It is to be presumed that the rubber was *raw* rubber, as the experiments were made in 1848.

<sup>3</sup> There was a tendency among elasticians at this comparatively early period in the development of elastic theory to assume that the transverse contraction,  $\mu$ , must be a simple fraction of the elongation,  $\lambda$ . Poisson had supposed  $\mu = \frac{1}{4}\lambda$ .



TABLE CLXIX

$L_0$  and  $D_0$  represent the original length and original diameter.

$L$  and  $D$  represent the length and the diameter after stretching.

$\sigma'$  represents the ratio of the diminution of diameter,  $\frac{D_0 - D}{D_0}$ , to the

increase of length,  $\frac{L - L_0}{L_0}$ , i. e.  $\frac{D_0 - D}{L - L_0} \cdot \frac{L_0}{D_0}$ .

Quantities in mms.

$L_0$	300	325	350	315	315	350	350	305	305	305	305	357
$L$	350	400	450	500	550	600	650	800	850	900	1000	1100
$D_0$	9.45	9.28	8.93	9.35	9.35	8.94	8.94	9.46	9.46	9.46	9.46	8.45
$D$	8.89	8.32	7.98	7.58	7.21	6.96	6.61	5.97	5.71	5.59	5.16	4.91
$\sigma'$	0.36	0.45	0.37	0.31	0.32	0.31	0.32	0.23	0.22	0.21	0.20	0.20
$\sigma$	0.40	0.53	0.45	0.47	0.47	0.46	0.50	0.48	0.49	0.49	0.51	0.48

*Increase of volume on stretching.*—Villari <sup>1</sup> made some measurements on the relation of transverse contraction to longitudinal extension, by means of hydrostatic weighing. He found a small but unmistakable increase of volume. The following table shows his results for a rubber cord, the initial length of which was 3.301 m., and the initial diameter 6.018 mm. The rubber was extended horizontally by means of a cord, passing over a roller, to which weights were attached. The elongation was measured by projecting, on to the floor, by means of light plumb lines, the distance between two gauge marks, three-quarters of the total length of the rubber apart. The projected distance was readily measured by a scale. The rubber, while under tension, was rolled round an iron plate. The specific gravity of the extended rubber was then determined by hydrostatic weighing; special care being taken to remove all air bubbles adhering to the rubber after its immersion. The diameter was calculated from the volume thus determined, together with the measured elongation.

TABLE CLXX

Load (kgs.).	Length (mm.).	Weight of water displaced (gms.).	Specific gravity.	Relative volume.	Calculated diameter (mm.).	Decrease of unit diameter ( $D_0 - D$ ).	Increase of unit length ( $L - L_0$ ).	$\sigma'$ .
0	3301.0 ( $L_0$ )	99.558	1.28120	1.00000	6.1968 ( $D_0$ )	—	—	—
2	5569.3 (L)	99.913	1.27665	1.00356	4.7794 (D)	0.2287	0.6872	0.333
5	9786.7 (L)	101.439	1.25744	1.01890	3.6328 (D)	0.4138	1.9648	0.211
7	13,209.3 (L)	103.050	1.23779	1.03510	3.1516 (D)	0.4914	3.0016	0.164

<sup>1</sup> *Cimento*, 1869, 28 (2) I, 332, 361; *Ann. der Phys.*, 1871, 143, 88, 290.

Villari agrees with Wertheim that  $\sigma'$  is approximately one-third for elongations below, say, 100 per cent., and diminishes rapidly with increased extension.

About the same time, Thomas,<sup>1</sup> experimenting with rubber thread of specific gravity 0.9794, reported that he found no increase in the volume of the rubber on extension. A piece of thread, 80 cms. long, weighing 1.25 gms., was wound on a brass frame and weighed in water; it was then stretched to five times its length and again weighed. No change in weight was observed, although the balance was sensitive to 0.5 mg. In a second experiment a ring, of 2 cms. internal diameter, and 8 gms. in weight, was placed over a copper plate,  $3 \times 8$  cms. No change in specific gravity could be recognized when the rubber was placed over the long dimension of the plate, as compared with its specific gravity when placed over the short dimension.

Villari states, in reference to Thomas's negative result, that he carried out twenty-four experiments and always found a diminution of the specific gravity on stretching. Possibly the difference between Villari's and Thomas's results may have lain in the circumstance that the former were obtained with a moderately mineralized compound and the latter with a pure gum compound. As, however, subsequent workers have observed a slight increase of volume on stretching pure gum compounds, it is perhaps more likely that the negative result of Thomas was due to the rubber used having been extended frequently prior to the experiment. Such extensions might, as Bouasse suggests, produce in the rubber a condition such that subsequent extension would not increase the volume.<sup>2</sup>

More recently Lundal,<sup>3</sup> applying the hydrostatic method to

<sup>1</sup> *Les Mondes*, 1869, 19, 575.

<sup>2</sup> That the history of a sample will influence its variation of volume on extension, is suggested by Bouasse (*J. de Physique*, 1903, 2, 494), whose observations on the influence of previous extensions on the tensile behaviour have already been described in Chapters X, XVIII and XIX. Bouasse supposes that, if the rubber sample the volume change of which is to be determined has, on the one hand, never been extended before, elongation may produce a marked and permanent change of density; and that, if, on the other hand, it has often been extended to a given length,  $L$ , "*il a pris pour tous les allongements compris entre 1 et  $L$  une certaine stabilité*," and that a future elongation will not alter its density. Between these two extremes there will, naturally, be intermediate conditions.

It may be noted that Schippel (see p. 499) found that "by working the rubber rings containing over fifty volumes of Barytes until the stiffness is removed" greater volume increases can be observed on extension than if the rings have not been worked.

<sup>3</sup> *Diss., Upsala*, 1897; *Ann. der Phys.*, 1898, 66, 741.

a pure gum compound, of specific gravity 0.90166 at 17.4°, and of sulphur-content 2.5-3 per cent., in the shape of strips 4.2 mm.<sup>2</sup> cross section, reported an increase of 0.45 per cent. in the volume on stretching by 22.9 per cent. He found that, if the rubber had previously absorbed paraffin oil, the volume increase shown by it was smaller. The first investigator to make exact measurements on the increase in volume of rubber on stretching was Joule.<sup>1</sup> Joule weighed bands of vulcanized rubber, stretched and unstretched, in water, and found, in a first experiment, that the specific gravity fell from 0.996057 to 0.994641, on stretching to twice the natural length. In a second experiment he found a decrease from 0.990918 to 0.988483 on stretching to 2.5 times the natural length. In each case the reduction in specific gravity was less than 0.2 per cent.

#### MODE OF CALCULATING POISSON'S RATIO. RÖNTGEN'S WORK

It will be observed that, as calculated by Wertheim and by Villari, Poisson's ratio for rubber is far from being constant. The merit of establishing the point of view from which the calculation of Poisson's ratio must be regarded in order that a constant value may be obtained lies with Röntgen.<sup>2</sup> Röntgen was led to take up the question because the small compressibility of rubber indicated a value not far removed from 0.5.<sup>3</sup> He determined  $\sigma$  from superficial measurements of the change in the ratio of the longitudinal to lateral dimensions of a rubber rod. The specimen used was a rod of approximately square cross section (30 × 28 mms.) and about 1.5 m. in length.<sup>4</sup> The specimen was suspended vertically, and was extended by loading weights on to a suitable arrangement at the lower end. At each point of extension a circle was stamped on the surface by means of a die (diameter, 21.67 mm.) provided with suitable marking ink. When the loads were removed from the rod, the circles had become ellipses. When elastic after-effect had ceased to produce any further change in the dimensions of the ellipses, their axes were measured carefully by means of a com-

<sup>1</sup> *Phil. Trans.*, 1859, **149**, 104.      <sup>2</sup> *Ann. der Phys.*, 1876, **159**, 601.

<sup>3</sup> Amagat, *C.R.*, 1884, **99**, 130-3, draws, from his experiments on the compression of rubber, the conclusion that  $\sigma$  is only slightly removed from 0.5.

<sup>4</sup> No information is given as to the composition of the rubber. And, it may be remarked, unless specifically stated otherwise, the same statement applies to all the other investigations on Poisson's ratio mentioned in the present chapter.

parator or dividing engine. From a knowledge of the axes of the ellipses, the longitudinal elongation and the lateral contraction at the load at which the ellipse was, as a circle, imprinted on the rubber is readily obtained. Thus:—

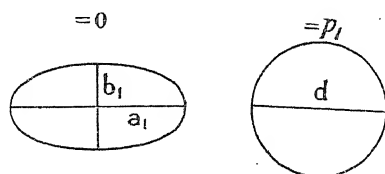


FIG. 48.

What appears, at load 0, as an ellipse with axes  $a_1$  and  $b_1$  was, at load  $p_1$  (say), a circle of diameter  $d$ . Hence the load  $p_1$  produced an elongation per unit length of  $\frac{d - b_1}{b}$  and a contraction per unit breadth of  $\frac{a_1 - d}{a_1}$ . If  $a_2$  and  $b_2$  represent the axes of the ellipse corresponding to the next higher load,  $p_2$ , then, for this increment of load, the increase in length is  $\frac{b_1 - b_2}{b}$ , and the diminution of unit breadth is  $\frac{a_2 - a_1}{a_2}$ . Thus we have, as the ratio of the increase of length to the diminution of breadth for the interval of extension corresponding to  $p_1 \rightarrow p_2$ ,

$$= \frac{(a_2 - a_1)b_2}{(b_1 - b_2)a_2}$$

The maximal extension in Röntgen's work was 32.3 per cent. The intervals between each measurement corresponded to elongations of 2-5 per cent. The values of  $\sigma$  given in the following table are calculated for each interval.

TABLE CLXXI

Elongation per unit length	0.031	0.074	0.109	0.145	0.175	0.235
$\sigma$	0.45	0.43	0.43	0.51	0.49	0.44
Increase of unit volume of unstretched rod	0.007	0.009	0.014	0.013	0.013	0.019

<sup>1</sup> More strictly, as Bouasse points out, the "original" length and breadth, to which the change of length and breadth over the interval should be referred, are not the length and breadth at end of the interval, but the mean length and breadth over the interval. That is, the formula should be written—

$$= \frac{(a_2 - a_1)}{(b_1 - b_2)} \cdot \frac{b_1 b_2}{a_1 a_2}$$

Knowing the axes of the ellipses, the volume of the rubber at the various extensions was calculated. If we consider a rectangular parallelepiped, corresponding to the ellipse of axes  $a_1$  and  $b_1$ , and having a volume  $a_1^2 b_1$ , we see that, when the rubber is under load  $p_1$ , it has become a cube, having a volume  $d^3$ . Hence, the increase of volume per unit volume of the unstretched rubber produced by the load  $p_1$  is  $\left(\frac{d^3}{a_1^2 b_1} - 1\right)$ .

It was expressly stated above that  $\sigma$ , which, within the limits of exactness of the experimental procedure used, is to be regarded as approximately constant, was calculated from the dimensional changes over each interval and not from the total dimensional change to a point in question. Röntgen pointed out that, in order to get values of the "constant"  $\sigma$  that were, actually, constant, it was necessary to derive it from the dimensional changes over small intervals only, and to take as the "original" length and section the actual length and section at the interval in question and not the unstrained length and section. He showed that it was failure to recognize this condition that had led other workers to obtain values for  $\sigma$  much less than 0.5 and diminishing greatly with increased elongation. He pointed out that, even if Poisson's ratio for rubber, as correctly defined, were strictly constant at 0.5, the method of calculation which derives the ratio from the total dimensional change over a long range will give values for  $\sigma'$  which rapidly diminish with increasing extension of the rubber. Thus:—

Taking  $l$  to represent the increase in unit length and  $b$  the increase of unit breadth of a rod of square cross section, then, assuming the volume to be constant ( $\sigma = 0.5$ ), the volume on extension will remain  $1 = (1 + l)(1 - b)^2$ , i. e.  $\frac{b}{l} = \sigma' = \frac{1}{l} \left(1 - \sqrt{\frac{1}{1 + l}}\right)$ .

Calculating from this formula values of  $\sigma'$  for various elongations, we get the following results:—

Elongation per unit length	0.001	0.03	0.5	1.0	2.0	3.0	4.0
$\sigma'$	0.4996	0.489	0.367	0.293	0.211	0.167	0.112 <sup>2</sup>

It would appear that in all cases where experimenters give values for Poisson's ratio for rubber considerably smaller than

<sup>1</sup>  $\sigma'$  may be used to designate Poisson's ratio as calculated from large dimensional changes.

<sup>2</sup> Schiller (*Ann. der Phys.*, 1907, **22**, 204) remarks that there is an error in Röntgen's calculation here—the figure should be 0.138.

0.5 and diminishing with increasing extension, the ratio has been calculated from dimensional changes over large extensions, and that in fact the values found do not vary greatly from the values (for  $\sigma'$ ) that would be calculated for the extensions in question, on the assumption, expressed by the above formula, that the volume does not change at all. Thus, *c. g.*, Röntgen points out that, for an elongation per unit length of 3.0016, Villari finds  $\sigma'$  to be 0.164 (*vide* Table CLXX), and that the value calculated according to the above formula is 0.167. Schiller<sup>1</sup> makes a similar observation with regard to Bjerkén's values for  $\sigma'$ . Bjerkén, by means of superficial measurements on a rubber band, found  $\sigma'$ , calculated for a series of extensions ranging from 23.3 to 413.5 per cent., to diminish from 0.403 to 0.125.<sup>2</sup> Schiller points out that, on the assumption that  $\sigma$  has a constant value of 0.48,<sup>3</sup>  $\sigma'$ , calculated, as Bjerkén calculated it, from the total dimensional changes at any point, would, in fact, have values close to those obtained by Bjerkén. For example: it would be 0.421 at 20 per cent.; 0.135 at 400 per cent. elongation. Bouasse<sup>4</sup> shows that a re-calculation of Wertheim's data according to the formula given below, also agrees with the view that  $\sigma$  approximates to 0.5 for small deformations. (See row 6, Table CLXIX.)

It can readily be seen that a modification of the methods of calculating the elastic constants suitable in the case of most materials must be made in the case of a material so deformable as rubber. The theory of elasticity concerns itself primarily with infinitely small deformations; and it is essentially to such deformations that the definitions of the elastic constants refer. The equations involving such constants can, in general, be applied directly to the measurements, of small deformations, which are usually made in the case of metals. They cannot, as what has gone before will have made clear, be so applied to the measurement of the great deformations which rubber is capable of undergoing. Cantone,<sup>5</sup> Bouasse,<sup>6</sup> O. Frank<sup>7</sup> and L. Schiller<sup>8</sup> have all, substantially, followed Röntgen's treatment, and have

<sup>1</sup> *Ann. der Phys.*, 1907, **22**, 204.

<sup>2</sup> The volumes increases recorded by Bjerkén are rather considerable.

<sup>3</sup> The value derived from Schiller's own measurements.

<sup>4</sup> *J. de Physique*, 1903, **2**, 492.

<sup>5</sup> *Rend. Ist. Lomb.*, 1898, **31**, (2), 1521 (*Beibl. Phys.*, 1899, **23**, 613; *Fortschr. Phys.*, 1898, **1**, 516).

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Ann. der Phys.*, 1906, **21**, 602.

<sup>8</sup> *Ibid.*, 1907, **22**, 204.

emphasized the necessity for referring  $\sigma$  to small deformations, if it is to be regarded as an elastic constant, and not merely (as is the case with  $\sigma'$ ) as an empirical expression of the relation of the lateral and longitudinal dimensions at a given extension.

Since, then,  $\sigma$  strictly refers to infinitely small dimensional changes, where finite changes are in question, it must be derived by integration,  $s$  being the cross section and  $l$  the length,  $\sigma = \frac{ds}{s} / \frac{dl}{l}$ . By integration we have  $\sigma = \log. \frac{s_1}{s_2} / \log. \frac{l_2}{l_1}$ .

*Values found for  $\sigma$  by superficial measurements.*—It will be observed from values of  $\sigma'$  tabulated on p. 492, that, on the assumption that  $\sigma$  is 0.5 for infinitely small deformations, its calculated value for an elongation of 3 per cent. is 0.489, or approximately 2 per cent. less than the limiting value. Röntgen corrects his experimental values, which were obtained with reference to elongations of 2–5 per cent. by similar percentages, and obtains, finally, as the mean value of,  $\sigma$ , 0.47. O. Frank,<sup>1</sup> from measurements, up to an elongation of 89.5 per cent., of the change of length and of breadth of a strip of rubber membrane, as determined between fine gauge lines on the surface, found a mean value for  $\sigma$  of 0.46. Schiller,<sup>2</sup> also by superficial measurements, up to an elongation of 101.21 per cent., obtained a value of 0.48. Schiller worked with strips, the breadth of which was moderately narrow compared with their length—say, 1 cm. compared with 25 cms. He points out that, if a broader strip is used, as was the case in Frank's experiments (Frank's strips were 10 × 40 cms.), there is a danger of the dimensions measured being affected to some extent by the clamping. In experiments with a broader strip, he obtained a value similar to Frank's value.

*Determination of  $\sigma$  by cubical measurements.*—The method (*a*", p. 487) of obtaining Poisson's ratio by a direct determination of the volume change on deformation by the use of an index liquid was first applied by Naccari and Bellati,<sup>3</sup> who, however, do not appear to have obtained very consistent results. It was employed by Pulfrich<sup>4</sup> in some determinations, the special interest of which is that they deal particularly with the period of tensile after-effect. A long tube, of internal diameter 5 mms., and wall thickness 5 mms., made of red rubber, was employed.

<sup>1</sup> *Loc. cit.*

<sup>3</sup> *Cimento*, 1877, 2 (3), 217.

<sup>2</sup> *Loc. cit.*

<sup>4</sup> *Ann. der Phys.*, 1886, 28, 87.

The upper end of the tube was closed by a capillary glass tube, and the lower end by a glass tube provided with a hook from which a balance-pan could be hung. The interior of the tube was filled with water. When a load was applied to the tube, it was found that the level of the water in the capillary connected with the interior fell, *i. e.* the volume of the tube increased. Observations of the fall of level in the capillary and of the increase of length of the rubber tube were continued, for in some cases fifteen days, during the period of after-effect. It was found that there was no essential distinction between the change of volume during the fore-strain and that during the after-strain. It was concluded, further, that the unit increase of volume ( $v/V_0$ ) was related to the load,  $p$ , and the unit elongation,  $l$ , in the following way— $v/V_0 = kl^p$ .  $\sigma$  was calculated for the small increments of length and volume during the periods of after-strain; the values found showed only small fluctuations and were on the average 0.456. The magnitude of the volume increase observed in Pulfrich's experiments was considerably larger than that which Villari had observed (p. 488). At the maximal elongation in question—151 per cent.—the increase of volume was 9.577 per cent.

Bouasse<sup>1</sup> points out a source of error in Pulfrich's procedure, *viz.* the increased hydrostatic pressure in the tube on extension. Thus, at an extension of 150 per cent., the lower part of the tube was subject to an extra pressure due to a height of more than 1 m. of water. (Original length of the tube: 75 cms.) The tube should have been immersed in water. Subsequent experimenters who have measured, by the displacement of level of an index liquid, the volume change of rubber on extension have always immersed the tube or rod in water.

Bouchet<sup>2</sup> has determined  $\sigma$  from measurements made, by the manometric method, at extremely small deformations. The deformations were brought about in the following ways: (a) By very small hydrostatic pressures in a rubber tube, filled with water, immersed in water, and connected with a capillary tube. The increments of pressure were only 0.213 mm. of water. (b) By extension of the same tube with loads of the order of 1 gm./cm.<sup>2</sup>. (c) By the electrostatic pressure produced on the rubber by two charged armatures, between which the rubber served as a dielectric. From (a) and from (b) the value obtained for  $\sigma$  was

<sup>1</sup> *Ann. de Phys.*, 1903, **2**, 492.

<sup>2</sup> *C.R.*, 1914, **158**, 1495, **159**, 470; 1915, **160**, 240.



0.495. In (c) the rubber, consisting of a pure gum compound, was in the form of a disc, 16 cms. in diameter and 0.6 cm. thick. The condenser was charged to a potential of 58.5 C.G.S. units. No change in volume whatever could be detected; and, having regard to the degree of sensitiveness of the apparatus, Bouchet concluded that  $\sigma$  for very small deformations could not differ from 0.5 by more than 0.00044.

*Poisson's ratio in different directions.*—A comparison of the value for  $\sigma$  obtained by superficial measurements with the value obtained for the same rubber by measurement of the volume change, *i. e.*, a comparison of the value of  $\sigma$  obtained from two-dimensional measurements with the value obtained by three-dimensional measurements, has led L. Schiller<sup>1</sup> to the significant conclusion that Poisson's ratio in rubber is different in different directions. Schiller found that the "dark Para rubber" sheet employed in his measurements of the change of dielectric constant with extension (see p. 483) gave, on calculating  $\sigma$  from measurements of the simultaneous change of the length and the breadth,<sup>2</sup> values for  $\sigma$ , *viz.* 0.538 and 0.530, which were noticeably greater than 0.5. As the measurements had been conducted with greater refinement even than in his previous determination of  $\sigma$  (p. 494), and as no other source of error could be detected,<sup>3</sup> he concluded that  $\sigma$  must have another value, less than 0.5, in the direction at right angles to the surface measured, so that the mean- $\sigma$ , which would be given by the volume change, would approximate more closely to 0.5 than the  $\sigma$  in either direction.

Direct determination of this  $\sigma$  (say,  $\sigma_{II}$ ), by measurement of the change of thickness of the sheet under tension was not feasible. But, by determining the mean- $\sigma$ , from the volume change,  $\sigma_{II}$  could be calculated. Schiller determined the mean- $\sigma$  by drawing out a piece of the sheet, 12  $\times$  8 cms., under water in a sealed vessel to which a capillary tube was attached. For an elongation of 25.95 per cent., the increase of volume, as indicated by the fall in level in the capillary tube, was 0.00831 c.c.; for an elongation of 21.58 per cent., 0.00607 c.c.  $\sigma'$  (*i. e.*,  $\sigma$  referred to the actual, finite extensions in question) for these two

<sup>1</sup> *Ann. der Phys.*, 1911, **35**, 931.

<sup>2</sup> Measured at fine gauge lines drawn on a white surface.

<sup>3</sup> The possibility of a slight concavity (*Einrollung*) being produced by the stretching and affecting the result was shown experimentally not to be an appreciable factor in the result.

elongations was 0.419 and 0.430 respectively.  $\sigma$  calculated<sup>1</sup> for infinitely small extensions from these data came out as 0.499 in both cases.

From this result for Poisson's ratio derived from the volume change and the result (0.535) derived from the superficial change of dimensions, the ratio for the thickness change could be calculated. For, if these three ratios are represented respectively by  $\sigma$ ,  $\sigma_I$  and  $\sigma_{II}$ , and the increase of unit length is represented by  $\lambda$ , we have for finite extensions

$$(1 - \sigma'_I \lambda) (1 - \sigma'_{II} \lambda) = (1 - \sigma' \lambda)^2,$$

that is

$$\sigma'_{II} = \frac{2\sigma' - \sigma'_I - \sigma'^2 \lambda}{1 - \sigma'_I \lambda}.$$

Putting  
i. e., since

$$\begin{aligned} \lambda &= 0, \text{ we get } \sigma_{II} = 2\sigma - \sigma_I, \\ \sigma &= 0.499 \text{ and } \sigma = 0.535, \\ \sigma_{II} &= 0.463. \end{aligned}$$

That is, Poisson's ratio for the rubber sheet in two directions perpendicular to one another was 0.535 and 0.463 respectively.

This result makes it appear that determinations of Poisson's ratio in rubber which have been made by various observers by superficial measurements have only a limited validity. They have been accepted as affording a value for  $\sigma$  in a cubical sense, on the assumption that the distribution of strain was uniform throughout the cross section: that the amount of contraction in any one direction was proportional to the amount of contraction in any other direction in the cross section. This assumption, however, now appears to be unacceptable.

*Influence of the character of the rubber "compound" on the increase of volume produced by extension.*—It must be considered as probable that the divergence of results shown among the results of the investigations mentioned above is ascribable, at least in part, to the fact that the magnitude of the volume increase on extension is influenced by character of the rubber and its previous history. But it is impossible to estimate the influence of these factors with any satisfaction from the investigations in question, as most of the investigations have been conducted by physicists, who, not unnaturally, have failed to appreciate the wideness of the range of mixtures included under the term

<sup>1</sup> From the formula  $\sigma = \frac{\lg \cdot [l_2 - \mu' (l_2 - l_1)] - \lg \cdot l_1}{\lg \cdot l_1 - \lg \cdot l_2}$ .

"rubber." In most of the investigations no particulars at all are given concerning the composition of the rubber used, and in none is the history of the specimens examined mentioned.

A study of the influence of a number of common compounding ingredients on the increase of volume produced by stretching has, however, recently been made by Schippel.<sup>1</sup> This study shows that the character of the compounding ingredients and their state of sub-division greatly affect the extent of the volume increase. In some cases the increase of volume was remarkably large. A volume increase of 120 per cent. at the breaking-point of a compound of 100 g. Para rubber, 30 g. litharge, 5 g. sulphur and 215 g. barytes, cured at 40 lb. steam pressure for thirty minutes, was indicated. A comparatively coarse ingredient, such as barytes, was found to lead to a much greater increase of volume than a very finely divided ingredient, such as carbon black. Schippel suggests that the result of extending a compounded rubber may suitably be pictured as involving the drawing away, in the direction of the extension, of the actual vulcanized caoutchouc from the mineral particles, around which, in the unextended state of the compound, it was closely apposed; with the result that empty spaces are formed near the particles.

The following is an account of Schippel's results: The various ingredients which were made the subject of study were added to a "base" consisting of 100 g. Fine Para, 30 g. litharge and 5 g. sulphur. Different volumes [ $1 \text{ volume} = (1 \times \text{the specific gravity of the ingredient}) \text{ g.}$ ] of different ingredients were added to this base. Each compound was vulcanized for thirty minutes at 40 lb. steam pressure. Its specific gravity in the unstretched state was determined, and then its specific gravity when stretched over a series of graduated steel bars.

The results would appear to be most suitably regarded from the following point of view, which is the point of view taken by Schippel: With smaller volumes of a compounding ingredient, the rubber, in most cases, "wets" the particles more or less completely; and the volume increase on stretching is small. When the volume of an ingredient is increased sufficiently, there is a tendency for agglomerations of particles to form—"the rubber surrounds groups of particles, instead of imbedding each particle individually"; and the volume increase on stretching rises considerably. In the case of barytes, no such comparatively

<sup>1</sup> "Volume Increase of Compounded Rubber under Strain."—*Jour. Ind. Eng. Chem.*, 1920, **12**, 33.

sudden rise in the volume increase is to be observed, because in this case the rubber "wets" the particles hardly at all—"there appears to be no cohesion whatever (or very little) between the rubber and the particles of barytes." In the case of barytes, even the smallest volume examined—5 volumes, led to an increase in volume (of 3 per cent. at an elongation of 150 per cent.); and in this case the increase of volume at a given elongation was, at all proportions of the ingredient, very approximately in direct proportion to the volume of the ingredient present.

In the case of whiting, the volume increases were small up to a proportion of 40 volumes; and beyond that proportion there was a sudden jump in the increase in volume on stretching, until, at a proportion of 150 volumes, the increase was almost equal to that produced by barytes, as may be seen from the following results:—

Proportion of ingredient (vols.) Volume increase per cent.	Whiting.			Barytes.		
	40	50	150	40	50	150
At 45% elongation	0.9	1.9	14.0	3.6	5.7	16.5
At 90%        ,,	2.8	6.2	—	9.5	14.1	36.5

In the case of zinc oxide, the growth of agglomerates occurs less easily than in the case of whiting. China Clay and Red Oxide, also, were studied, but only in proportions up to 25 or 30 volumes. The volume increases with such proportions were small only. At 100 per cent. elongation 25 volumes of China Clay led to a volume increase of 1.71, and 25 volumes of Red Oxide to a volume increase of 0.51 per cent., as compared with a volume increase of 0.22 per cent. for the base without any addition. In the case of lampblack the volume increase up to a 50-volume content of the pigment was small only; but it appeared that beyond this proportion the rubber was unable to wet each particle separately and that agglomeration began, with the result that the increase of volume at an elongation of 45 per cent. was 0.33 per cent. for the 50-volume compound, and 2.12 per cent. for the 75-volume compound. Observations on carbon black were made on compounds containing up to 30 volumes of the pigment. It appeared that the rubber absorbed this volume readily and wetted it uniformly. The following approximate figures, taken from Schippel's curves, indicate the magnitude of the volume increase with different ingredients, when 30 volumes of them were present. Percentage increase of volume at an extension

of 150 per cent.: base (without additions), 0.37; with barytes, 13.6; with whiting, 3.5; with zinc oxide, 0.4; with lampblack, 1.41; with carbon black, 1.01.

It would appear that the question of the magnitude of volume increase on stretching compounded rubber is closely bound up with the size of the particles of the compounding ingredients, whether in their original or in their agglomerated condition. Of the ingredients mentioned above, barytes is the coarsest and carbon black the finest.<sup>1</sup> The average particle of whiting has only one-eighth the volume of the average particle of barytes. Hence, in order that the whiting in the 150-volume compound might, as was observed to be the case, lead to almost the same volume increase as barytes, it would be necessary that the particles should be agglomerated into groups having eight times multiples of eight times the volume of the barytes particles agglomerates.

Of several suggestive aspects which this study presents, mention may be made of the bearing which in Schippel's work it has on the phenomena of hysteresis. Schippel remarks that the "agglomeration of pigment particles and the phenomena connected with it are of vital importance, since the sudden growth of agglomerated particles at certain volumes may be coincident with a rapid increase of hysteresis, due to the friction when the rubber body is distorted amongst those particles which are in dry contact with one another."

At a certain proportion of the compounding ingredient the volume increase at the breaking-point (estimated by extrapolation) would appear to be maximal. The maximum was clearly to be recognized within the limits of the experiments in the case of barytes and in the case of whiting. In the former case the maximum occurred in the compound containing 50 volume per cent. This showed an ultimate elongation of about 550 per cent., and an estimated volume increase at the breaking-point of 122 per cent. In the case of whiting the maximum occurred in the 100-volume compound. This showed an ultimate elongation of about 375 per cent., and a volume increase at the breaking-point of 83 per cent.

*Demonstration of change of volume on stretching.*—Mention may be made of a simple method, employed by W. B. Wiegand and H. F. Schippel, for demonstrating the diminution of specific gravity produced by stretching rubber. A band of a suitable

<sup>1</sup> Zinc oxide behaves somewhat abnormally, due, possibly, to its being chemically passive in the vulcanization process.

rubber compound, of, say, specific gravity 1.5, is placed round the edge of an oval or rectangular slab of wax, of such dimensions that the circumference corresponds to an elongation of the rubber band to two or more times its unstrained length, and of such mass that, when the rubber band is stretched round it, it will just float in water. The wax and its circumscribing ring are placed in a tall cylinder of water. They float on the water. The ring is then removed from the circumference of the wax and is placed across the short dimension of the wax, so that it is no longer strained. If the wax and its ring are now replaced in the cylinder, they will be seen to sink.

#### CUBICAL COMPRESSIBILITY OF RUBBER

It is commonly stated that, although highly deformable, rubber is little if any more compressible than water.<sup>1</sup> It would seem, however, so far as the available data go, that the compressibility of rubber varies considerably with the character of the rubber compound, and that in the case of pure gum-sulphur compounds it may be considerably greater than the compressibility of water.

Claperyon<sup>2</sup> reported the compressibility of a sample examined by him as  $92.95 \times 10^{-6}$  of its original volume per kg./cm.<sup>2</sup> pressure, *i. e.* approximately double the compressibility of water. Amagat<sup>3</sup> compared the compressibilities of rubber and bronze in a differential form of Regnault's piezometer. He concluded that the compressibilities of the two materials were substantially the same. Mallock<sup>4</sup> records determinations of the volume elasticity of three different samples of rubber. The samples were placed in a vertical glass tube, on the drawn-out neck of which a ball of soft wax and turpentine mixture was placed. The tube was immersed in water in a cast-iron cylinder, and was subjected to a pressure of *ca.* 550 lb./in.<sup>2</sup>. The volume of the filament of wax which was thus intruded into the tube represented the volume by which the rubber had been compressed. The results obtained were as follows:—

#### Volume elasticity (lb./in.<sup>2</sup>.)

- |  |         |
|--|---------|
| 1. Soft, grey rubber (sp. gr., 1.289; $P_b = 820$ lb./in. <sup>2</sup> ;<br>$L_b = 990$ per cent.)             | 198,000 |
| 2. Red rubber (sp. gr., 1.407; $P_b = \text{ca. } 820$ lb./in. <sup>2</sup> ;<br>$L_b = 730$ per cent.)        | 115,000 |
| 3. Hard, grey rubber (sp. gr., 2.340; $P_b = \text{ca. } 820$<br>lb./in. <sup>2</sup> ; $L_b = 440$ per cent.) | 940,000 |

<sup>1</sup> This statement seems to be due to an expression of opinion to this effect in Thomson and Tait's *Elements of Natural Philosophy*.

<sup>2</sup> *C.R.*, 1858, 46, 112.

<sup>3</sup> *C.R.*, 1884, 99, 130.

<sup>4</sup> *Proc. Roy. Soc.*, 1889, 46, 245-7.

As determined in the same apparatus, the volume elasticity of water was 296,000 lb./in.<sup>2</sup>.

Lundal,<sup>1</sup> working with a "pure, black rubber," of specific gravity 0.90166 at 17.4° and sulphur-content 2.5-3 per cent., determined the cubical compressibility over a range of pressures. For these determinations the rubber was placed in a piezometer along with water. Only relative figures are given in reporting the results. Taking the coefficient of compressibility of water between 0.5 and 6 atmospheres as, in convenient, defined units, 0.037, the coefficient of compressibility of the rubber ( $\alpha$ ) at various pressures is shown in the following table:—

TABLE CLXXII

Temperature, 17°

Pressure in atmospheres)	0.615	1.188	1.699	2.230	2.776	3.227	3.834	4.326	4.940	5.386
$\alpha$	9.54	9.25	9.04	8.32	7.83	7.44	6.73	6.13	5.65	5.21

The variation of the coefficient with pressure is given closely by the equation  $\alpha = 10.063 - 0.7060 P - 0.0333 P^2$ . It would appear from Lundal's results that at pressures of about 1 atmosphere a pure gum-sulphur compound is about 250 times as compressible as water. It would also appear that the compressibility diminishes very much more rapidly with increase of pressure than in the case of water.

Lundal also made some observations on the influence on the compressibility of rubber of its absorption of paraffin oil. The rubber was placed in the piezometer along with paraffin oil; and its compressibility was determined at intervals. In the following table the change in compressibility ( $\alpha_1$ ) as the absorption of the oil proceeded is shown in the same units as those used in the preceding table.

TABLE CLXXIII

Time . .	0 h.	15 m.	18 h.	30 m.	24 h.	40 h.	43 h.	47 h.	68 h.	89 h.	118 h.	160 h.	168 h.
$\alpha_1$		11.48	12.24	13.97	18.62	6.68	4.06	2.06	0.75	0.49	0.28	0.05	

The compressibility first increases up to the point at which the density of the rubber has reached a minimum; following on this the compressibility quickly falls, while the density increases. (The changes of compressibility are much greater than the changes of density.) Finally, when, Lundal conceives, the pores or intermolecular interstices of the rubber have been filled, the rubber becomes almost incompressible.

<sup>1</sup> *Ann. der Phys.*, 1898, 66, 741.

## BIBLIOGRAPHY

(In cases where the title of a paper is given both in Dutch and in English, a summary in English accompanies the original Dutch paper.)

- ADRIANI, A. *Verhandeling over de Gutta-percha en Caoutchouc en derselver verhandeling, etc.* Utrecht, 1850.
- AHRENS, F. *Ein Beitrag zur Kenntnis der Kautschuklösungen.* Chem. Ztg., 1910, 34, 266-7.
- . *Ein Beitrag zur Kenntnis der kolloiden Natur des Kautschuks.* Chem. Ztg., 1912, 36, 505-6.
- . *Ein Beitrag zur Kenntnis der Vulkanisation des Kautschuks.* Gummi-Ztg., 1913, 28, 490.
- . *Oxidation of Caoutchouc.* Chem. Abstrs., 1914, 1351. (Original: *Kunststoffe*, 3, 478.)
- ALEXANDER, P. *Die Nitrosite des Kautschuks und deren Verwendung für die Analyse von Roh-Kautschuk und Kautschukproducten.* Ber., 1905, 38, 181-4; Ber., 1907, 40, 1070-8; Zeit. angew. Chem., 1911, 24, 680-7.
- . *Zur Frage der Entschwefelung von vulkanisiertem Kautschuk.* Koll. Zeit., 1912, 10, 252-3; Chem. Ztg., 1912, 36, 1289-91, 1340-2, 1358-9.
- ALEXROD, S. *Ueber Löslichkeit verschiedener Kautschuksorten in Benzin.* Gummi-Ztg., 1905, 19, 1053-6; 20, 105.
- . *Methode zur direkten Bestimmung des Kautschukgehaltes in vulkanisierten Kautschukmischungen.* Gummi-Ztg., 1907, 21.
- . *Ueber die direkte Kautschukbestimmung in Weichgummiwaren.* Chem. Ztg., 33, 895.
- . *Ueber die Viscosität von Kautschukquellungen.* Gummi-Ztg., 1909, 23, 810-11.
- . *Ueber die Chloralhydratmethode.* Gummi-Ztg., 1909, 23, 845.
- . *Beitrag zur Erklärung des Vulkanisationsprozesses.* Gummi-Ztg., 1909, 24, 352-4.
- AMAGAT, E. H. *Sur la valeur du coefficient de Poisson relative au caoutchouc.* C.R., 1884, 99, 130-3.
- ARCHBUTT, L. *The Preparation of Rubber for Analysis.* Analyst, 1913, 38, 559-64.



- ARENS, P. *Bacterium prodigiosum* (Ehrenb.) *Lehm. et Neum. als Erreger der roten Flecken auf frisch bereiteten Kautschuk*. Cent. Bakt., 1912, 35 (2 Ab.), 465-6.
- . *Handleiding voor de Bereiding van Rubber*. Mededeelingen van het Proefstation Malang, No. II. (1915).
- . *Schimmels en bacteriën op bereide rubber*. Rubber Recueil, 1914, pp. 397-8. (*Pilze und Bakterien auf bereitetem Kautschuk*. Ibid., pp. 399-400).
- . *Eenige proeven ter voorkoming van "rustiness" bij sheets en enkele opmerkingen omtrent "greasiness."* Archief, 1917, 1, 197-202. (*Occurrence of Rustiness and Greasiness on Sheets*. Ibid., 203.)
- . *Eenige aan de praktijk ontleende cijfers omtrent den invloed van het uitdunnen op de productie van Heveatuinchen*. Archief, 1917, 1, 234-40. (*Thinning-out*. Ibid., 241.)
- . *Zijn aan het tappen driptins voordeelen verbonden*. Archief, 1919, 3, 36-41. (*Does tapping with drip-tins give any advantage?* Ibid., 42.)
- ARISZ, W. H. *Over de factoren, die het uitlooeien van de latex bepalen bij Hevea brasiliensis*. Archief, 1918, 2, 347-356. (*On the factors which influence the latex flow from Hevea brasiliensis*. Ibid., 357-60.)
- and VAN VLISSINGEN, L.R.E.S. *Over den invloed van zwaar tappen op de chemische samenstelling van de latex*. (*The influence of heavy tapping on the chemical composition of the latex*.) Archief, 1920, 4, 27-31.
- D'ARSONVAL. *Action de quelques gaz sur le caoutchouc*. C.R., 1899, 128, 1545-6.
- ASHTON, A. W. *Note on the Electrification of Dielectrics by Mechanical Means*. Phil. Mag., 1901, 2 (6), 233-5; Proc. Phys. Soc., 1901, 17, 751-4.
- AUSTERWEIL, G. *Sur le passage de l'hydrogène à travers le tissu caoutchouté des aérostats*. C.R., 1912, 154, 196-8.
- BAKER, T. J. *The Frequency of Transverse Vibrations of a Stretched Indiarubber Cord*. Phil. Mag., 1900, 49 (5), 347-51; Proc. Phys. Soc., 1900, 17, 107-112.
- BALLAND. *Veränderung des vulkanisierten Kautschuks beim Aufbewahren*. Jour. Pharm. Chim., 1887, 15 (5), 417-18.
- BAMBER, M. K. *Rubber Manuring Experiments at the Experiment Station, Peradeniya*. Dept. Agric. Ceylon, Bull. No. 18, 1915. 12 pp.
- BANCROFT, K. *The Spotting of Plantation Para Rubber*. Dept. Agric. F.M.S., Bull. No. 16, 1913. 30 pp.
- BARR, G. *Rubbered Balloon Fabrics*. Rubber Industry, 1914, 259-75.
- BARRITT, N. W. *On the Coagulation of the Latex of Hevea brasiliensis, and its Bearing on the Strength of Rubber*. J. Soc. Chem. Ind., 1914, 33, 289-93; Rubber Industry, 1914, 130-6.

- BARROWCLIFF, M. *Theory of the Coagulation of Hevea Latex*. J. Soc. Chem. Ind., 1918, **37**, 48-50T.
- . "Standard" Plantation Rubber. J. Soc. Chem. Ind., 1918, **37**, 95-8T.
- . *The Planning of Manurial Experiments*. Rep. Batavia, 136-43; Agric. Bull. F.M.S., 1914, **3**, 1-6.
- . *The Acidity of Malayan Soils*. Agric. Bull. F.M.S., 1914, **3**, 45-50.
- , BUNTING, B., AND SPRING, F. G. *Manuring Experiments on Castleton Estate*. Agric. Bull. F.M.S., 1914, **3**, 111-14.
- BARUS, K. *The Solution of Vulcanized Rubber*. Amer. J. Sc. & Arts (Silliman), 1891, **42**, 359-69.
- BARY, P. *Application de l'osmose à la deresinification et à la regeneration des Caoutchoucs*. Eighth Internat. Cong. Appd. Chem., 1912, Vol. IX, 7-15.
- . *Sur le mode de dissolution des matières colloïdales*. C.R., 1911, **152**, 1386-7.
- . *Valeur approchée du poids moléculaire du caoutchouc*. C.R., 1912, **154**, 1159-60.
- . *The Estimation of Free Sulphur in Vulcanized Rubber*. Chem. Zentralbl., 1913, II, 81-3. (Original: Moniteur Scient., 1913, **3** (5) I, 301-8; Rev. gen. chim. pure et appl., 1913, **16**, 142-5.)
- , AND WEYDERT, L. *Caractère apparemment réversible de la réaction de vulcanisation du caoutchouc par le soufre*. C.R., 1911, **152**, 676-8.
- BASKERVILLE, C. *Note on the Preparation of Rubber Samples for Analysis*. J. Amer. Chem. Soc., 1906, **28**, 1511.
- BATESON, E. *The Tapping of the Para Rubber Tree. Some Physiological Experiments*. Dept. Agric. F.M.S., Bull. No. 23, 1914. 54 pp.
- BAUR, E. *Die Fortschritte der Vererbungs-forschung und ihre Bedeutung für die Züchtung tropischer Kulturpflanzen, besonders der Kautschukpflanzen*. Rep. Batavia, 1914, XXX-XLVIII.
- BECKER, R. *Einiges über das Kautschuktetrabromid nach Hübener*. Gummi-Ztg., 1911, **25**, 331, 598.
- BEADLE, C., AND STEVENS, H. P. *Vulcanization Tests with Plantation Rubbers*. Chem. News, 1907, **96**, 37-9.
- . *The so-called "Nerve" of Rubber*. Chem. News, 1907, **96**, 247-8.
- . *Mode of Valuing Raw Rubber*. Chem. News, 1908, **97**, 73-4.
- . *A Machine for the Mechanical Testing of India-rubber*. J. Soc. Chem. Ind., 1909, **28**, 1111-2.
- . *The Influence of Mineral Ingredients on the Properties of Rubber*. J. Soc. Chem. Ind., 1911, **30**, 1421-5.
- . *Note on the Influence of Re-working Typical Para Rubbers*. J. Soc. Chem. Ind., 1911, **30**, 1425-6.

- BEADLE, C., AND STEVENS, H. P. *Some Analyses of Hevea Latex*. Analyst, 1911, **36**, 6-9.
- . *Raw Rubber Testing*. Rubber Industry, 1911, 265-84.
- . *Impact-Tensile Tests on Rubber and a Comparison with Tensile and Hysteresis Tests*. Rubber Industry, 1911, 344-50.
- . *Acidity of Raw Rubbers*. I.R.J., 1911, **51**, 713-14.
- . *An Investigation into the Nature and Properties of Hevea Latex*. Eighth Internat. Cong. Appd. Chem., 1912, **9**, 17-43. (Also in German: Koll. Zeit., 1913, **13**, 207-22.)
- . *The Nitrogenous Constituent of Para Rubber and its Bearing on the Nature of Synthetic Rubber*. J. Soc. Chem. Ind., 1912, **31**, 1099-1103.
- . *Der sogenannte "unlösliche" Bestandteil des Kautschuk und sein Einfluss auf die Qualität desselben*. Koll. Zeit., 1912, **11**, 61-5.
- . *The Nature of the Resinous Constituent of Rubber*. Eighth Internat. Cong. Appd. Chem., 1912, **25**, 581-6.
- . *Method of Determining the Amount of Insoluble Particles in Raw Rubber*. Analyst, 1912, **37**, 13-16.
- . *Die unlöslichen Bestandteile von Ceara- und Ram-bong-Kautschuk*. Koll. Zeit., 1913, **12**, 46-8.
- . *The Production of Rubber of Uniform Colour*. Rubber Recueil, 1914, pp. 357-60.
- . *Alkali Treatment of Coagulum*. I.R.J., 1916, **51**, 713-14.
- BEADLE, C., STEVENS, H. P., AND MORGAN, S. *Sodium Bisulphite in the Manufacture of Rubber*. I.R.J., 1913, **46**, 222-3.
- BEDFORD, C. W., AND SCOTT, W. *Reactions of Accelerators during Vulcanization*. Jour. Ind. Eng. Chem., 1920, **12**, 31-33.
- BELFIT, M. W. *A Method for the Direct Estimation of the Rubber in a Compound*. J. Ind. Eng. Chem., 1916, **8**, 326-7.
- BEMMELEN, VAN B. *On the Climate of the Principal Rubber-producing Countries*. Rubber Recueil, 1914, pp. 145-60.
- BERNARD, C. *Over de physiologische beteekenis van den latex. Teysmannia (Java)*, 1918, **29**, 523.
- BERNSTEIN, G. *Studien über die Vulkanisation des Kautschuks*. Koll. Zeit., 1912, **11**, 185-91; 1913, **12**, 193-7, 273-7.
- . *(Isolation of the Insoluble Constituent of Rubber)*. Koll. Zeit., 1914, **15**, 49-50.
- . *Vulcanization*. Rubber Industry, 1914, 164-71.
- BIERER, J. M. *An Autographic Friction-testing Machine for Testing Mechanical Rubber Goods*. Proc. Amer. Soc. for Testing Materials, 1914, **14** II, 627-38.
- BIFFEN, R. H. *The Functions of Latex*. Anns. Bot., 1897, **11**, 334-9.
- . *The Coagulation of Latex*. Anns. Bot., 1898, **12**, 166-71.

- BIFFEN, R. H. *Methods of Preparing India-Rubber*. J. Soc. Arts, 1898, 47, 111-14.
- BING, K. *Das Leimigwerden des Rohgummis*. Koll. Zeit., 1909, 5, 260-1.
- BISHOP, O. F., GRANTHAM, J., AND KNAPP, M. D. *Probable Error in Field Experimentation with Hevea*. Archief, 1917, 1, 335-64.
- BJERKÉN, V. P. *Untersuchung der durch Druck und Zug hervorgerufenen Doppelbrechung bei Kautschuk und Leimgallerten*. Ann. der Phys., 1891, 43, 808-16.
- . *Ueber die Analogie zwischen Kautschuk und Leimgallerten in Bezug auf Elasticität und Wärme*. Ann. der Phys., 1891, 43, 817-30.
- BOBILOFF, W. *Algemeene inleiding tot het onderzoek over de physiologische rol van de latex bij Hevea brasiliensis*. Archief, 1918, 2, 281-313.
- . *Het verband tusschen de anatomie van den bast en de productie bij Hevea brasiliensis*. Archief, 1918, 2, 488-515. (*The Relationship between the Anatomical Structure of the Cortex and the Yield of Hevea brasiliensis*. *Ibid.*, 516-17.)
- . *De Samenhang tusschen de bladeren en het melksap van Hevea brasiliensis*. Archief, 1918, 2, 735-66. (*The Relationship between the Leaves and the Latex of Hevea brasiliensis*. *Ibid.*, 767-8.)
- . *Onderzoekingen over de vorming van latex bij Hevea brasiliensis*. Archief, 1919, 3, 374-404. (*Investigations Regarding the Formation of Latex in Hevea brasiliensis*. *Ibid.*, 405-7.)
- BOBILOFF, W. SR. *De reactie van Hevea-latex*. Archief, 1919, 3, 408-10. (*The Reaction of the Latex of Hevea brasiliensis*. *Ibid.*, 411.)
- BOGGS, C. R. *Vulcanization of Rubber by Selenium*. J. Ind. Eng. Chem., 1918, 10, 117-18.
- BOILEAU, P. *Note sur l'élasticité du caoutchouc vulcanisé*. C.R., 1856, 42, 933-7.
- BOLAS, T. *The India-rubber and Gutta-percha Industries*. J. Soc. Arts, 1880, 28, 753-60, 763-7, 773-9, 783-9, 803-8.
- BOLTZMANN, L. *Einige experimente über den stoss von cylindern*. Sitzungsber. Wien, 1881, 84 (II Ab.), 1225-9; Ann. der Phys., 1882, 17, 343-7.
- BORROWMAN, A. T. *Viscosity of Hevea Latex at Various Dilutions*. Rubber Industry, 1911, 243-7.
- BOUASSE, H. *Sur le coefficient  $\sigma$  de Poisson pour le caoutchouc vulcanisé*. J. de Physique, 1903, 490-8.
- . *Sur l'amortissement des trépidations du sol par les suspensions en caoutchouc*. J. de Physique, 1904, 3 (4), 511-24.
- . *Sur les modules d'élasticité de traction du caoutchouc vulcanisé*. Ann. de la Faculté des Sciences de Toulouse, 1904, 6 (2), 177-276.

- BOUASSE, H., ET CARRIÈRE, Z. *Sur le module de traction et la coefficient de dilatation du caoutchouc vulcanisé.* C.R., 1903, 136, 1130-1.
- . *Sur les courbes de traction du caoutchouc vulcanisé.* Annales de la Faculté des Sciences de Toulouse, 1903, 5 (2), 257-83.
- . *Sur la reactivité du caoutchouc vulcanisé.* Annales de la Faculté des Sciences de Toulouse, 1903, 5 (2), 285-321.
- BOUCHET, L. *Nouvelles déterminations du coefficient de Poisson relatif au caoutchouc vulcanisé.* C.R., 1914, 159, 470-3.
- . *Sur un dispositif manométrique pour l'étude des très petites déformations du caoutchouc.* C.R., 1914, 158, 1495-8.
- . *Déformation du caoutchouc vulcanisé sous l'action d'un champ électrostatique.* C.R., 1915, 160, 240-2.
- . *Sur les variations d'épaisseur d'une lame de caoutchouc sous l'influence d'un champ électrostatique.* C.R., 1916, 163, 479-81.
- . *Recherches expérimentales sur les déformations électriques des diélectriques.* Ann. de Physique, 1919, 13, 303-442.
- BOURN, A. O. *A New Rule of Vulcanization.* Rubber Industry, 1914, 411-16.
- BOUTARIC, J. *L'industrie du caoutchouc.* Soc. des Ingénieurs civile de France, Procès-Verbaux de la Séance du 19 Fev., T II.
- BRET, C. M. *Sur l'existence en Afrique occidentale de deux formes stables d'Hevea brasiliensis Mull. Arg. présentant une aptitude différente à la production du latex.* Le Caoutchouc, 1913, 7291-2.
- BREUIL, P. *Application du microscope à l'examen du caoutchouc.* C.R., 1905, 140, 1142-3.
- . *Les essais mécaniques du caoutchouc manufacturé.* Le Caoutchouc, 1905, 2, 6.
- . *The Mechanical Testing of India-rubber.* Lects. on Rubber, 1908, pp. 294-303.
- . *Vulcanisation du caoutchouc.* Le Caoutchouc, 1911, 8, 5298-5306.
- . *Essais de caoutchouc d'Afrique.* Le Caoutchouc, 1913, 6884-91.
- . *Quelques essais nouveaux exécutés avec le dynamomètre système Pierre Breuil.* Le Caoutchouc, 1914, 11, 8347-55; 1915, 8585-7.
- BRITLAND, W. J., AND POTTS, H. E. *The Use of Pyridine in Rubber Analysis.* J. Soc. Chem. Ind., 1910, 29, 1142-3.
- BROCKENDEN. *New Application for Caoutchouc.* Literary Gazette, No. 1220; Year-book of Facts in Science and Art, London, 1841, 75-6.
- . *On the Application of Caoutchouc to Different Manufactures, and Particularly to Elastic Web.* J. Franklin Inst., 1833, 280-3.

- BROCKENDEN. *On Some Properties Peculiar to Caoutchouc, and their Applications.* J. Franklin Inst., 1851, 22 (3), 68-9; Athenæum, London, April 1851.
- BROWN, H. *Rubber, its Sources, Cultivation, and Preparation.* London, 1914. 245 pp. (Murray.)
- BRYCE, G., AND CAMPBELL, L. E. *On the Mode of Occurrence of Latex Vessels in Hevea brasiliensis.* Dept. Agric. Ceylon, Bull. No. 30, 1917. 22 pp.
- BUDDE, T. *Zur Bestimmung des Reinkautschuks in Kautschukwaren.* Veröff. aus den Gebiete des Militär-Sanitätswesens, 1905, Heft 29. (Chem. Zentralbl., 1905, II, 173.)
- . *Ueber die Wertbestimmung des vulkanisierten Kautschuks.* Gummi-Ztg., 1907, 21, 1265-8.
- . *Zur Bestimmung des Kautschuks als Tetrabromid.* Gummi-Ztg., 1908, 22, 33-4, 955-6.
- . *Ueber Wertbestimmungen kalt vulkanisierter Kautschukwaren nach dem "Tetrabromidverfahren."* Mitt. a.d. Gebiete des Militärsanitätswesen, 1909, Heft 41, Tl. 3, 70-83. (Chem. Zentralbl., 1909, II, 1017.)
- . *Ueber ein neues Verfahren, den gebundenen Schwefel im vulkanisierten Kautschuk zu bestimmen.* Gummi-Ztg., 1909, 23, 1143-4.
- . *Zur Bestimmung des Kautschuks als Tetrabromid.* Gummi-Ztg., 1909, 24, 4-6; 1910, 25, 269-70.
- BUNSCHOTEN, W. *Vulcanizatie zonder zwavel volgens Ostromyslenski.* Chem. Weekblad, 1918, 15, 257-68. (*Vulcanization without Sulphur according to Ostromyslenski.* I.R.J., 1918, 56, 719-24.)
- BUNTING, B. *Dynamite Experiments.* Agric. Bull. F.M.S., 1915, 3, 337-41.
- . *Manuring Experiments on Rubber.* Agric. Bull. F.M.S., 1916, 4, 125-39.
- . *Liming Experiments.* Agric. Bull. F.M.S., 1916, 4, 373-80.
- BUREAU OF STANDARDS. *Circular of the Bureau of Standards, No. 38, The Testing of Rubber Goods.* Washington. 3rd edit., 1915. 89 pp.
- BURGHARDT, C. A. *The India-rubber Manufacture.* J. Soc. Chem. Ind., 1883, 2, 119-22.
- BYSOW, B. *Zur theorie der Kaltvulkanisation.* Koll. Zeit., 6, 281-3; J. Russ. Phys.-Chem. Soc., 42, 638-46.
- . *Zur theorie der Heissvulkanisation.* Koll. Zeit., 7, 160-1; J. Russ. Phys.-Chem. Soc., 42, 1358-62.
- . *Zur Kenntnis der Kaltvulkanisation.* Koll. Zeit., 1911, 8, 47-8, 209.
- CALVERT, A. *The Laticiferous Tissue in the Stem of Hevea brasiliensis.* Ann. Bot., 1887, 1, 75-7.

- CAMPBELL, L. E. *Tapping and the Storage of Plant-Food in Hevea brasiliensis*. Dept. Agric. Ceylon, Bull. No. 16, 1915. 26 pp.
- . *Physiological Effects Produced in Hevea brasiliensis by Various Tapping Systems*. Dept. Agric. Ceylon, Bull. No. 19, 1915. 27 pp.
- . *Seasonal Variations in the Storage of Plant-Food in Hevea brasiliensis and Their Relation to Resting Periods*. Dept. Agric. Ceylon, Bull. No. 22, 1915. 18 pp.
- . *Measurements of "Bark Renewal" in Hevea brasiliensis*. Dept. Agric. Ceylon, Bull. No. 33, 1917. 24 pp.
- . *Preliminary Note on the Natural Coagulation of the Latex of Hevea brasiliensis*. J. Soc. Chem. Ind., 1917, 36, 274-5.
- CANTONE, S. C. M. *Sulla trazione del caucciù*. Rendic. Ist. Lomb. di Scienze, 1898, 31 (2), 1521-48. (Beibl. Phys., 1899, 23, 613; Fortschr. Phys., 1898, 54 (1), 516.)
- . *Sul coefficiente di Poisson per il caucciù*. Riposta ad Nota del Sign. Bouasse. Cimento, 1903, 6 (5), 91-2; Rend. Lomb., 1903, 36 (2), 873-8. (Beibl. Phys., 1904, 28, 1051.)
- . *Sulla elettrostrizione*. Riposta ad una nota del sig. More. Milano, Rend. Ist. Lomb., 1901, 34 (2), 1095-1101. (Fortschr. Phys., 1902, II, 437.)
- CANTONE, M., AND CONTINO, G. *Sulla torsione del caucciù*. Rend. Ist. Lomb., 1899, 32 (2), 189-202. (Beibl. Phys., 1899, 23, 614; Fortschr. Phys., 1899, 55 I, 502.)
- . *Contributo allo studio delle proprietà fisiche del caucciù*. Cimento, 1900, 12 (4), 242-57.
- . *Sulla dilatazione termica del caucciù*. Rend. Ist. Lomb., 1900, 33 (2), 215-26. (Sc. Abstrs., 1901, 473.)
- CASPARI, W. A. *The Composite Nature of Raw India-rubber*. J. Soc. Chem. Ind., 1913, 32, 1041-3.
- . *The Osmotic Pressure and Physical Constitution of Caoutchouc Solutions*. Trans. Chem. Soc., 1914, 105, 2139-50.
- . *India-rubber Laboratory Practice*. London, 1914. (Macmillan.)
- . *The Behaviour of Colloids Towards Pure and Mixed Liquids. Part I. The Systems Caoutchouc-Benzene-Alcohol and Caoutchouc-Benzene-Acetone*. Trans. Chem. Soc., 1915, 107, 162-71.
- CAYLA, V. *Recherches préliminaires sur les diastases oxydantes des latex*. Comptes rendus Soc. Biol., 1908, 65, 128.
- . *The Diastases in Latex*. I.R.J., 1910, 39, 563-4.
- CEYLON, DEPARTMENT OF AGRICULTURE. *Vulcanization Tests at the Imperial Institute on Samples of Rubber prepared by L. E. Campbell*. Dept. Agric. Ceylon, Bulls. Nos. 23, 24, 27, 32, 35 (1916-18).
- CHAMPION, P. *Sur la Dambonite et le Dambose nitrée*. C.R., 1871, 73, 114-15.

- CHÈNEAU, O. *Allgemeiner Gang zur Untersuchung des Kautschukwaren.* Zeit. Nahr.-Genussm., 1900, 3, 312-18.
- CHÈNEVEAU, C., AND HEIM, F. *Sur l'extensibilité du caoutchouc vulcanisé.* C.R., 1911, 152, 320-2.
- . *The Extensibility of Vulcanized Rubber.* Rubber Industry, 1911, 327-35.
- . *Elasticimètre enregistreur. Application à l'étude de l'extensibilité du caoutchouc.* J. de Physique, 1912, 2 (5), 535-50.
- CLAPEYRON. *Mémoire sur le travail des forces élastique dans un corps solide élastique déformé par l'action de forces extérieures.* C.R., 1858, 46, 208-12.
- CLAUBRY, GAULTIER DE H. *Des moyens propres à déterminer l'existence du chlorure de soufre ou de ses éléments dans le caoutchouc.* C.R., 1859, 49, 245-6.
- . *Addition à la recherche du chlore dans le caoutchouc.* C.R., 1859, 49, 361-7.
- CLIGNETT, P. S. *Electrische coagulation.* Rubber Recueil, 1914, 374-6. (*Electrical Coagulation.* Ibid., 377-9.)
- CLOËZ, S., AND GIRARD, A. *Note sur la présence du chlore et du soufre dans le caoutchouc naturel ou manufacturé.* C.R., 1860, 50, 874-6.
- COHEN, N. H. *Ueber Phytosterine aus Afrikanischem Rubber.* Arch. der Pharm., 1908, 246, 515-20.
- . *Ueber Lupeol.* Arch. der Pharm., 1908, 246, 520-2.
- . *Ueber einige Phytosterine aus sogenanntem S. Afrika-Rubber.* Arch. der Pharm., 1908, 246, 592-3.
- DE LA CONDAMINE. *Sur la résine élastique nommée caoutchouc.* Histoire de l'Académie Royale des Sciences, 1751, 17-22.
- . *Sur une résine élastique, nouvellement découverte à Cayenne par M. Fresneau; Et sur l'usage de divers sucres laiteux d'arbres de la Guinée ou France équinoxiale.* Mémoires de l'Académie Royale des Sciences, 1761, 319-33.
- COOMBS, G. E. *Report on the Question of Field Experiments, with Special Reference to the Execution of Tapping Experiments on Estates.* Agric. Bull. F.M.S., 1916, 4, 229-42.
- AND GRANTHAM, J. *Field Experiments and the Interpretation of their Results.* Agric. Bull. F.M.S., 1916, 4, 206-16.
- CORBINO, O. M. *Sulla variazione della costante dielettrica del caoutchouc con la trazione. Riposta a una nota del Dote-Ercolini.* Cimento, 1902, 3 (5), 85.
- CORBINO, O. M., AND CANNIZZO, F. *Sulla variazione della costante dielettrica del caoutchouc per la trazione.* Rend. Linc., 1898, 7 (5), 286-93. (Fortschr. Phys., 1898, II, 427-8.)
- CORPORAAL, J. B. *Tap en tapproeven op Sumatra's Oostkust. VIII. Bastverbruik met het tapmes-"Bosch."* Archief, 1918, 2, 278-9. (*Tapping and Tapping-Experiments on the East Coast of Sumatra. VIII. Bark-Consumption by the Bosch-knife.* Ibid., 280.)



- CRAMER, P. J. S. *Wild Rubber and Selection*. Rubber Recueil, 1914, 13-32.
- . *Seed Selection of Hevea*. Rep. Batavia, 22-38.
- CRANOR, D. F. *The Effect of Organic Accelerators on the Vulcanization Coefficient*. I.R.W., 1919, 61, 137-140.
- CROSSLEY, W. *Coagulation of Rubber by means of Acetic Acid*. I.R.J., 1911, 41, 1205-7.
- . *Adsorption of Acid by the Colloids of Dialysed Hevea Latex*. I.R.J., 1911, 42, 1293-4, 1341-2.
- DANGIN, A. *The Composition of Caoutchouc*. J. Russ. Phys.-Chem. Soc., 30, 843-51. (Chem. Zentralbl., 1899, I, 295.)
- DAVIES, C. *A Sketch of the History and Properties of Caoutchouc*. J. Franklin Inst., 1830, 123-5.
- DAVIES, E. L. *Hysteresis Tests for Rubber*. J. Ind. Eng. Chem., 1914, 6, 985-6; J. Soc. Chem. Ind., 1914, 33, 992-3.
- DEBONNEFROY, E. *Note sur le caoutchouc vulcanisé et sur son emploi comparé à celui de l'acier fondu pour les ressorts des voitures et wagons dans les chemins de fer*. Soc. Ing. Civ. Mém., 1854, pp. 86-95.
- DEKKER, P. *De bepaling en de beteekenis van het zoogenaamde "onoplosbare deel" van ruwe rubber*. Meded. Delft, 1916, 483-519.
- . *Eene vlugge en een vondige bepalingmethode van het harsgehalte in rubber*. Meded. Delft, 1916, 520-2.
- . *Bepaling van het gehalte aan onverzeepbare harsbestanddelen van verschillende rubbersoorten*. Meded. Delft, 1916, 527-8. (Gummi-Ztg., 1917, 31, 824.)
- . *Onderzoek, verricht met geconserveerde latex*. Meded. Delft, 1916, 529-37.
- . *The Determination of Sulphur in Vulcanized Rubber*. I.R.J., 1920, 59, 413-18.
- DEMOGET. *Electricité du caoutchouc*. Les Mondes, 1873, 31, 509. (Repertorium, 9, 272-3; Dingler's Polyt., 212, 160.)
- DENIER AND VERNET, G. *Étude bactériologique de la coagulation naturelle du latex d'Hevea brasiliensis*. C.R., 1917, 165, 123-6.
- DEUSSEN, E. *Eine quantitative Bestimmung des Schwefels im Kautschuk*. Zeit. angew. Chem., 1913, 26, Aufsatz, 494-6.
- DIETZEL, C. F. *Ueber die Elasticität des vulcanisierten Kautschuks und Bemerkungen über die Elasticität fester Körper überhaupt*. Polyt. Centralbl., 1857, 689-94. (Fortschr. Phys., 1857, 13, 143-4.)
- DITMAR, R. *Ueber das Verhalten des Rohkautschuks gegen concentrirte Salpetersäure*. Ber., 1902, 35, 1401-2.
- . *Die Einwirkung von Radiumstrahlen auf Kautschuk*. Gummi-Ztg., 1904, 19, 3-4.
- . *Einige theoretische Bemerkungen zur Untersuchungsmethode zur Ermittlung des Reinkautschukgehaltes in Kautschukartikeln nach Joseph Torrey*. Gummi-Ztg., 1905, 20, 204.

- DITMAR, R. *Zur Chemie des Kautschuks*. Chem.-Ztg., 1905, **29**, 175-6.
- . *Die kolloidisierende Wirkung des Kautschuks auf Selen*. Gummi-Ztg., 1905, **19**, 766-7.
- . *Der Schwefelkohlenstoff als quellungsmittel für Kautschuk*. Gummi-Ztg., 1905, **19**, 578-81.
- . *Ueber quellungsmittel für trockenen, mastizierten Parakautschuk*. Gummi-Ztg., 1905, **19**, 831-3.
- . *Die zusammensetzung des Latex verschiedener kautschukpflanzen mit Rücksicht auf die Bildung des Kautschuks in der Pflanze (Ein Beitrag zum Kautschuksynthese)*. Gummi-Ztg., 1905, **19**, 901-3.
- . *Ueber die Löslichkeit des bloss mit Schwefel vulkanisierten Kautschuks und von Kautschukwaren in Pyridin und über Essigester als Lösungsmittel für Kautschukharze*. Gummi-Ztg.
- . *Eine neue Methode der Rohkautschukbestimmung*. Gummi-Ztg., 1906, **20**, 364-6.
- . *Ueber den Einfluss des Schwefelgehaltes auf die Reissfestigkeit bei der Heissvulkanisation des Parakautschuks*. Gummi-Ztg., 1906, **20**, 394.
- . *Ueber die Harzgehalt einiger Rohkautschuksorten*. Gummi-Ztg., 1906, **20**, 394.
- . *Die praktische Bedeutung der Untersuchungsmethode zur Ermittlung des Reinkautschuks nach Joseph Torrey*. Gummi-Ztg., 1906, **20**, 418.
- . *Theorie der Kautschukvulkanisation im Lichte der Harrieschen Kautschukformel als physico-chemisches Problem betrachte*. Koll. Zeit., 1906, **1**, 167-70.
- . *Influence of Cold Vulcanization upon the Tensile Strength and Elasticity of Para Rubber*. (J. Soc. Chem. Ind., 1906, **25**, 435. Original: Gummi-Ztg., 1906, **20**, 678-9.)
- . *Effect of Zinc Oxide on the Vulcanization and the Oxidation of India-rubber*. (J. Soc. Chem. Ind., 1906, **25**, 1107. Original: Gummi-Ztg., 1906, **20**, 103-4.)
- . *Influence of Chalk and of Moisture on the Vulcanization of India-rubber*. (J. Soc. Chem. Ind., 1906, **25**, 326. Original: Gummi-Ztg., 1905, **20**, 579-80.)
- . *Laboratory Method of Testing the Durability of Rubber and Rubber Goods*. (J. Soc. Chem. Ind., 1906, **25**, 383. Original: Gummi-Ztg., 1906, **20**, 628.)
- . *Relation between Specific Gravity and Sulphur-content of Vulcanized Para Rubber*. (J. Soc. Chem. Ind., 1906, **26**, 487. Original: Gummi-Ztg., 1906, **20**, 733.)
- . *Effect of Heavy Magnesia as a Filling Material upon India-rubber*. (J. Soc. Chem. Ind., 1906, **25**, 487. Original: Gummi-Ztg., 1906, **20**, 760.)
- . *Influence of Light Magnesia as a Filling Material upon India-rubber*. (J. Soc. Chem. Ind., 1906, **25**, 597. Original: Gummi-Ztg., 1906, **20**, 816.)

- DITMAR, R. *Vulcanization on India-rubber in the presence of Litharge.* (J. Soc. Chem. Ind., 1906, **25**, 821. Original: Gummi-Ztg., 1906, **20**, 1077-8.)
- . *The Absorption of Gases through Rubber Tubes.* I.R.J., 1907, **34**, 85-6, 197-8.
- . *Ueber die Vulkanisationsgeschwindigkeit, Reissfestigkeit und Oxydation verschiedener Kautschuksorten bei verschiedenem Atmosphärendruck.* Chem.-Ztg., 1907, **31**, 638-9.
- . *Determination of Sulphur in Rubber and Rubber Substitute by Dennstedt's (Combustion) Method.* (J. Soc. Chem. Ind., 1907, **26**, 212. Original: Gummi-Ztg., 1907, **21**, 497.)
- . *Influence of Barium Sulphate on the Vulcanization and Oxidation of Rubber.* (J. Soc. Chem. Ind., 1907, **26**, 159. Gummi-Ztg., 1907, **21**, 418-19.)
- . *Influence of Pressure on the Rate of Vulcanization, Strength and Oxidation of Different Kinds of Rubber.* (J. Soc. Chem. Ind., 1907, **26**, 882. Original: Chem.-Ztg., 1907, **31**, 638-9.)
- . *Influence of the Washing-water on Rubber.* (J. Soc. Chem. Ind., 1907, **26**, 104. Original: Gummi-Ztg., 1907, **21**, 392-3.)
- . *On the Absorption and Diffusion of Gases through India-rubber, and the Application of these Processes in Aerial Navigation.* Lects. on Rubber, 1908, 207-30.
- . *Die Analyse des Kautschuks, der Gutta-percha, Balata und ihrer Zusätze.* Wien u. Leipzig, 1909, 288 pp.
- . *Welchen praktischen Wert haben mechanische Prüfungen des Kautschuks?* Koll. Zeit., 1912, **10**, 238-42.
- . *Paraflecken. Eine kolloidchemische Erscheinung.* Koll. Zeit., 1912, **11**, 36-7.
- . *Das Färben von Kautschuk mit organischen Farben.* Gummi-Ztg., 1913, **28**, 203-4. (Le Caoutchouc, 1914, **11**, 7951-2.)
- . *Die Technologie des Kautschuks.* 1915.
- . *Vulkanisationsbeschleuniger.* Gummi-Ztg., 1915, **29**, 424.
- AND DINGLINGER, O. *Effect of Powdered Glass on the Vulcanization and Oxidation of Rubber.* (J. Soc. Chem. Ind., 1907, **26**, 25. Original: Gummi-Ztg., 1907, **21**, 234-5.)
- AND THIEBEN, R. *Die Veränderungen der wichtigsten anorganischen Kautschukfüllstoffe durch die Dampfvulkanisation.* Koll. Zeit., 1911, **11**, 77-80.
- . *Schwindflecken am vulkanisierten Kautschuk. Eine kolloidchemische Erscheinung.* Koll. Zeit., 1911, **11**, 80-3.
- AND WAGNER, A. *Influence of the Resin-content on the Combined Sulphur in India-rubber.* (J. Soc. Chem. Ind., 1906, **25**, 996. Original: Gummi-Ztg., 1906, **20**, 1280-2.)
- DONATH, E. *Ueber Kautschuk und Gutta-percha.* Zeit. angew. Chem., 1892, 43-5.
- DOUTY, D. E. *Some American Methods of Testing Mechanical Rubber Goods.* Rubber Industry, 1914, 230-45.

- DRABBLE, E. AND SPENCE, D. *Effect of Varying Atmospheric Conditions on the Resin-content of India-rubber. Preliminary Communication.* Quart. Jour. Inst. Comml. Research Tropics, Liverpool, 1, 119.
- DUBOSC, A. *Histoire du caoutchouc.* Le Caoutchouc, 1913, 10, 6859-75, 7083-7100, 7155-67, 7265-78, 7577-7606; 1914, 11, 8023-32, 8566-8; 1916, 13, 8956-9.
- . *Étude sur la turgescence des caoutchoucs.* Le Caoutchouc, 1917, 14, 9265-7.
- . *Dé vulcanisation par les vitaliseurs.* Le Caoutchouc, 1918, 15, 9568.
- . *Dé vulcanisation du caoutchouc par formation de l'hexaméthylène tetramine dans la gomme.* Le Caoutchouc, 1918, 15, 9588-90.
- AND LUTTRINGER, A. *Le Caoutchouc, sa Chimie nouvelle, ses Synthèses.* Paris, 1913. (Eng. trans., 1918, Griffen.)
- DUCCA, W. A. *Testing Methods of Rubber Contents in Raw and Vulcanized Rubber.* J. Ind. Eng. Chem., 1912, 4, 372-4.
- DUNSTAN, W. R. *Note on the Constituents of the Seeds of the Para Rubber Tree (Hevea brasiliensis).* Proc. Chem. Soc., 1907, 168-9.
- EATON, B. J. *The Preparation of Plantation Para Rubber.* Dept. Agric. F.M.S., Bull. No. 17, 1912.
- . *The Viscosity of Rubber Solutions.* Agric. Bull. F.M.S., 1913, 2, 9.
- . *Note on a Latex Hydrometer.* Agric. Bull. F.M.S., 1914, 2, 224-6.
- . *Methods of Coagulation and Preparation of Plantation Para Rubber.* Internat. Rubber Congress, Batavia, 1914. (Pamphlet).
- . *Preliminary Note on a new Rapidly-vulcanizing Rubber.* Agric. Bull. F.M.S., 1914, 4, 30-3.
- . *Vulcanization Experiments. The Effect of Mixing different Raw Rubbers.* Agric. Bull. F.M.S., 1915, 4, 4-6.
- . *The Smoking of Plantation Rubber.* Agric. Bull. F.M.S., 1915, 3, 428.
- . *On the Action of Alkalis and Acids on Rubber.* Agric. Bull. F.M.S., 1916, 4, 162-7.
- . *Rubber Adulterated with Starch.* Agric. Bull. F.M.S., 1916, 4, 300-1.
- . *The Effect of Vacuum drying Crêpe Rubber.* Agric. Bull. F.M.S., 1916, 4, 219-21.
- . *Chinese Vinegar as a Coagulant.* Agric. Bull. F.M.S., 1916, 4, 321-2.
- . *New Researches on the Variability of Plantation Para Rubber.* J. Soc. Chem. Ind., 1917, 36, 1217-26.
- . *Notes on the Preparation of Raw Rubber with Special*

- Reference to "Slab" Rubber and Variability. Agric. Bull. F.M.S., 1917, 5, 183-8.
- EATON, B. J. *The Preparation of Plantation Para Rubber with Special Reference to Future Considerations.* Agric. Bull. F.M.S., 1917, 5, 372-80.
- . *Note on the Development of Chromogenic Organisms in Dry Raw Rubber allowed to become Damp.* Agric. Bull. F.M.S., 1917, 6, 177-9.
- . *The Anaerobic Coagulation of Hevea latex.* Agric. Bull. F.M.S., 1917, 6, 156-8.
- . *Effect of Drying "Slab" Rubber under different Conditions.* Agric. Bull. F.M.S., 1918, 6, 315-6.
- AND DAY, F. W. F. *The Distribution of Nitrogen in Coagulum and Serum of Hevea Latex on Coagulation with Acetic Acid.* Agric. Bull. F.M.S., 1916, 4, 350-3.
- . *A Preliminary Investigation on the Estimation of Free and Combined Sulphur in Vulcanized Rubber, and the rate of Combination of Sulphur with different Types of Plantation Para Rubber.* J. Soc. Chem. Ind., 1917, 36, 16-20.
- . *Further Experiments on the Combined Sulphur Content of Slow and Fast Vulcanizing Plantation Para Rubber.* J. Soc. Chem. Ind., 1917, 36, 1116-19.
- . *Ageing Experiments on Vulcanized Plantation Para Rubber.* J. Soc. Chem. Ind., 1919, 38, 339-47 T.
- AND GRANTHAM, J. *Vulcanization Experiments on Plantation Para Rubber. The Cause of Variability.* J. Soc. Chem. Ind., 1915, 34, 989-999; Agric. Bull. F.M.S., 1915, 3, 175-203.
- . *On the Coagulation of Hevea Latex and a New Method of Coagulation.* Agric. Bull. F.M.S., 1915, 4, 26-30.
- . *Vulcanization Experiments on Plantation Rubber. The Extent of Variability Caused by Lack of Uniformity in Factory Methods.* Agric. Bull. F.M.S., 1915, 3, 218-25.
- . *The Nitrogen Content of Rubber and its Relation to the Rate of Vulcanization.* Agric. Bull. F.M.S., 1915, 4, 1-4.
- . *Vulcanization Experiments on Plantation Rubber.* Agric. Bull. F.M.S., 1915, 4, 58-62.
- . *Vulcanization Experiments on Plantation Para Rubber, II. The Cause of Variability and some Contributory Factors.* J. Soc. Chem. Ind., 1916, 35, 715-28.
- . *Variability of Plantation Para Rubber with different Technical Mixings.* J. Soc. Chem. Ind., 1916, 35, 1046-50.
- , GRANTHAM, J. AND DAY, F.W.F. *The Preparation and Vulcanization of Plantation Para Rubber.* Dept. Agric. F.M.S., Bull. No. 27, 1918. 398 pp.
- AND WHITBY, G.S. *Notes on the Preparation, by the Distillation and by the Combustion of Wood, of Acid Coagulants, and on their Effect on the Quality of Rubber.* Agric. Bull. F.M.S., 1917, 5, 124-34.

- EDUARDOFF, F. *Beitrag zur Frage über die Präexistenz des Kautschuks im Latex*. Gummi-Ztg., 23, 809.
- EDWARDS, J.D. AND MOORE, I.L. *Notes on Cemented Seams and Rubber Cements*. I.R.J., 1919, 57, 599-604.
- ERCOLINI, G. *Variazione della costante dielettrica del cauciu con la trazione meccanica*. Cimento, 1901, 2 (5), 297-301; Riv. sci. industr., Firenze, 1902, 34, 49. (Beibl. Phys., 1903, 27, 69; Fortschr. Phys. 1901, II, 401.)
- . *Sulla variazione della costante dielettrica del caoutchouc con la trazione*. Cimento, 1902, 3 (5), 85.
- . *L'elettrostrizione del cauciu*. Cimento, 1905, 10 (5), 185-191. (Beibl. Phys., 1906, 30, 503; Sc. abstrs., 1906 A, 92-3.)
- ERDMANN, H. *Ueber Thiozonide, ein Beitrag zur Kenntnis des Schwefels und seiner ringförmigen Verbindungen*. Annalen, 1908, 362, 133-73.
- ESCH, W. *Application of the Bromide-derivative Methods for the Assay of Vulcanized Rubber Wares*. (Abstrs. Chem. Soc., 1911, ii, 946. Original: Chem.-Ztg., 1911, 35, 971-2.)
- AND CHWOLLES, A. *Beitrag zur Frage der Präexistenz des Kautschuks im Latex*. Gummi-Ztg., 1905, 19, 165-6.
- ESENBECK, N. v. AND MARQUART, C. *Ueber den Milchsaft der Feigenbäume, Viscin und Cautschuk*. Annalen, 1835, 14, 43-50.
- EXNER, F. *Ueber die Abhängigkeit der Elasticität des Kautschuks von der Temperatur*. Sitzungsber. Wien, 1874, 69, 102-14; Ann. der Phys., 1874, 153, 62-75.
- EYMER, A. *Abhängigkeit der Dielektricitätsconstants von mechanischen und thermischen Einwirkungen*. Diss. Marburg, 1906 (iv-1-44).
- FARADAY, M. *On Pure Caoutchouc, and the Substances by which it is Accompanied in the State of Sap or Juice*. Quart. Jour. Soc. London, 1826, 21, 19-28.
- FARMER, J. B. *Science and the Rubber Industry*. J. Soc. Arts, 1918, 66, 490-6.
- FAWSITT, C. A. *Chloride of Sulphur: its Properties and Relations, with Especial Reference to its Use as a Vulcanizer, and its Analysis*. J. Soc. Chem. Ind., 1886, 5, 638-41.
- . *The Vulcanization of India-rubber, with Special Reference to the Use of Chloride of Sulphur*. J. Soc. Chem. Ind., 1889, 8, 368-77.
- . *The "dry heat" Vulcanization of Rubber, with Special Reference to the Use of an Improved Vulcanizer*. J. Soc. 1891, 11, 332-6.
- FENDLER, G. *Ueber die neueren Methode der Kautschukuntersuchung, speziell in ihrer Anwendung auf Rohkautschuk*. Ber. Dtsch. pharm. Ges., 1904, 14, 215-8.

- FENDLER, G. *Ueber das Verhalten des Kautschuks gegen einige Lösungsmittel und über Rohkautschukuntersuchung.* Gummi-Ztg., 1904, **19**, 41-5.
- . *Ueber die Untersuchung des Rohkautschuks.* Gummi-Ztg., 1910, **24**, 931; **25**, 311-6, 351-7, 530.
- FENDLER, G. AND KUHN, O. *Neue Studien über Kautschuk und Kautschukuntersuchung.* Gummi-Ztg., 1908, **22**, 132-4, 160-3, 215-9, 249-52.
- . *Zur Bestimmung des Kautschuks als Tetrabromid.* Gummi-Ztg., 1908, **22**, 710-3.
- FESSENDEN, R. A. *The Laws and Nature of Cohesion.* Science, 1892, **20**, 48-52; 1913, **21**, 113-5; Chem. News, 1892, **66**, 206, 217; 1893, **68**, 204.
- . *Some Recent Work on Molecular Physics.* J. Franklin Inst., 1896, **142**, 187-216.
- FICKENDY, E. *Die sogenannte Coagulation des Kautschuks.* Koll. Zeit., 1910, **8**, 43-7.
- . *Zur Erklärung des Wundreflexes bei der Kautschukgewinnung.* Koll. Zeit., 1910, **8**, 157-8.
- . *Die Verhütung des Klebrigwerdens von Rohkautschuk.* Koll., 1911, **11**, 81-3.
- FICKER, E. *Experimentelle Untersuchungen über die Dielektrizitätsconstante von Gemischen.* Ann. der Phys., 1910, **31** (4), 365-91.
- FITTING, H. *Physiologische Grundlagen zur Bewertung der Zapfmethoden bei Kautschukbäumen.* Tropenpflanzen, 1909, **13**, Beiheft, Nr. 2, 1-43.
- FLACK, M., AND HILL, L. *The Imbibition of Rubber.* Proc. Jour. Physiology, 1910, **40**, xxxiii.
- FLEURY, R. DE. *Le Caoutchouc brut.* Le Caoutchouc, 1913, 7071-83.
- FLINT, E. R. AND TOLLENS, B. *Notizen über Oxycellulose und über Bornesit.* Annalen, 1893, **272**, 288-90.
- FOL, J. G. *On the Relationship between the Amount of Resins and the Viscosity of Rubber Solutions.* 8th Internat. Cong. Appl. Chem., 1912, **9**, 71-3. (Also in Dutch: Meded. Delft, 1916, 321-4.)
- . *Bepaling der viscositeit van rubberoplossingen.* Meded. Delft, 1912, 22-53; Chem. Weekblad, **10**, 154-74. (*Viscositeitsbestimmung von Kautschuklösungen.* Koll. Zeit., 1913, **12**, 131-47.)
- . *On the Desirability of International Testing Methods for Raw Rubber.* Rubber Recueil, 1914, 437-59. (Also in Dutch: Ibid., 411-36.)
- . *The Results of Scientific Testing and of the Empirical Appreciation of Raw Rubber.* Rep. Batavia, 1914, 179-90. (Also in Dutch: Meded. Delft, 1916, 214-27.)
- . *Eenige opmerkingen over de bepaling der viscositeit van rubberoplossingen.* Meded. Delft, 1916, 325-9.

- FOL, J. G. *Chemische en mechanisch-technische rubberonderzoekingen*. Meded. Delft, 1916, 284-99.
- FOL, J. G. AND DEKKER, P. *Overzicht der voornaamste methoden door den Voorlichtingsdienst toegepast bij chemisch onderzoek*. Meded. Delft, 1916, 347-56.
- AND VAN HEURN, F. C. *De invloed van den vulcanisatietijd, de vulcanisatietemperatuur en de hoeveelheid toegevoegde zwavel op de eigenschappen van ge vulcaniseerde rubber*. Meded. Delft, 1916, 330-46.
- FOURCROY. *Sur le sur qui fournit la Gomme élastique*. Ann. de Chim., 1791, 11, 225-236.
- FOX, C. P. *The Effect of Copper on Crude Rubber*. J. Ind. Eng. Chem., 1917, 9, 1092-3.
- FRANK, F. *On the Physical Testing of India-rubber by Schopfer's New Apparatus*. Lects. on Rubber, 1908, 289-93.
- . *Beitrag zur Klärung der Frage der Ursache des Klebrigwerdens von Rohgummi*. Gummi-Ztg., 1910, 25, 39-40.
- . *India-rubber Research*. Rubber Industry, 1911, 301-5.
- . *Viscosity Determinations*. (J. Soc. Chem. Ind., 1911, 30, 560. Original: Gummi-Ztg., 1911, 25, 990-2.)
- . *The Proteids in Caoutchouc and in Latex*. Rubber Industry, 1914, 144-8.
- AND GNÄDINGER. *Urukuri Nut: Chemical Composition of the Kernel and of the Distillate from the Woody Portion*. (J. Soc. Chem. Ind., 1910, 29, 891. Original: Gummi-Ztg., 1910, 24, 1328-9.)
- AND MARCKWALD, E. *Ein Beitrag zur Analyse von Kautschukwaren*. Chem.-Ztg., 1902, 26, 385.
- . *Verfahren zur direkten, exakten Bestimmung der Mineralbestandteile in Kautschukwaren zur Angestaltung der Kautschukanalyse*. Gummi-Ztg., 1908, 22, 1344-6.
- . *Die Chloralhydratmethode*. Gummi-Ztg., 1909, 23, 979.
- . *Das Leimigwerden des Rohgummis. Einige einleitende Versuche zur Klärung der Ursache dieser Erscheinung*. Koll. Zeit., 1909, 5, 189-91.
- . *Verfahren zur direkten Bestimmung der stickstoffhaltigen Nebenbestandteile im Rohkautschuk*. Gummi-Ztg., 1912, 26, 936-7.
- . *The Action of Copper and Other Metals on Rubber and Rubber Compounds. I. The Deterioration of Cable Insulations due to Insufficient Vulcanization*. (J. Soc. Chem. Ind., 1914, 33, 653; Original: Gummi-Ztg., 1914, 28, 1280-3.)
- FRANK, O. *Die Analyse endlicher Dehnungen und die Elastizität des Kautschuks*. Ann. der Phys., 1906, 21, 602-8.
- FREEMAN, W. G. *The Adaptability under Cultivation of the Para Rubber Tree*. Lects. on Rubber, 1908, 147-52.
- FRITZ, F. *Para Seed Oil*. (J. Soc. Chem. Ind., 1914, 33, 33; Chem. Abstrs., 1914, 1019. Original: Rev. Fett- und Harz-Ind., 20, 295.)



- FRÖHLICH, E. H. *Beiträge zur mechanischen Prüfung von Kautschukwaren.* Gummi-Ztg., 1912, **26**, 1050-3.
- GALLAGHER, W. J. *The Significance of Branching in young Hevea Trees.* Rep. Batavia, 1914, 68-78.
- GARDNER, H. C. T. *On the Physical Constitution of Caoutchouc-bearing Latexes, and the Relation of the so-called "Coagulation" thereto.* Rubber Industry, 1911, 225-30.
- GAUNT, R. *The Viscosity of Rubber Solutions.* J. Soc. Chem. Ind., 1914, **33**, 446-52.
- . *The Determination of Sulphur in Rubber.* Analyst, 1915, **40**, 9-11.
- GAUTIER, C. M. *Pneumatic Tyre Strains.* I.R.J., 1919, **57**, 393-7.
- GEE, W. W. H. AND TERRY, H. L. *On the Specific Heat of Non-conductors. Part I. Caoutchouc.* Memoirs Manchester Lit. & Phil. Soc., 1891, **4** (4), 38-46.
- GEER, W. C. *Accelerated Life of Rubber Compounds (Symposium, Rubber Section, Amer. Chem. Soc.),* I.R.W., 1916, **55**, 127-30.
- GIRARD, A. *Note sur un nouveau principe, volatil et sucré trouvé dans le caoutchouc de Gabon.* C. R., 1868, **67**, 820-5.
- . *Sur un nouveau principe, volatile et sucré, trouvé dans le caoutchouc de Bornéo.* C. R., 1871, **73**, 426-9.
- . *Sur une nouvelle matière sucré volatile, extraite du caoutchouc de Madagascar.* C. R., 1873, **77**, 995-8.
- GLADSTONE, J. H. AND HIBBERT, W. *The Optical and Chemical Properties of Caoutchouc.* Trans. Chem. Soc., 1888, **53**, 679-88.
- . *On the Molecular Weight of Caoutchouc and other Colloidal Bodies.* Phil. Mag., 1889, **28** (5), 38-42.
- GORDON, J. E. H. *Measurements of Electrical Constants. No. II. On the Specific Inductive Capacities of Certain Dielectrics.* Phil. Trans., 1879, **170**, 417-46.
- GORTER, K. *Verdere gegevens over het pekkigworden.* Meded. over Rubber, No. II, 1912. 56 pp.
- . *Sur le glucoside des graines de l'Hevea brasiliensis Mull.* Arg., Rec. trav. chim., 1912, **31** (3), 264-6.
- . *Brechet pekkigworden.* Meded. over Rubber, No. I, 1911.
- . *Tackiness of Rubber.* Rubber Recueil, 1914, 385-90.
- . *De viscositeitsindex.* Meded. over Rubber, No. IV, 1915. 51 pp.
- . *Over de chemische Samenstelling van Hevea-latex.* Archief, 1917, **1**, 374-7.
- AND SWART, N. L. *Eenige ervaringen over het goaguleeren van Hevea-latex zonder azijnzur.* Meded. v. h. Rubberproefstation West-Java, 1916, No. 6, 1-24. (English account: *The Coagulation of Latex in the Presence of Sugars.* Agric. Bull. F.M.S., 1916, **5**, 48-52.)
- GOTTLOB, K. O. *Ueber die Einwirkung der Salpetrigen Säure auf Kautschukarten.* Zeit. angew. Chem., 1907, **20**, 2213-21.

- GOTTLOB, K. O. *Ueber Vulkanisations-Beschleuniger*. Gummi-Ztg., 1916, 30, 303, 326.
- GOUGH, J. *A Description of a Property of Caoutchouc or India-rubber; with some Reflections on the Cause of the Elasticity of this Substance*. Manchester Philosophical Memoirs, 1805, 1 (2), 288-295; Nicholson's Jour., 1806, 13, 305.
- GOULIER, C. M. *Dilatation du caoutchouc*. Les Mondes, 1869, 20, 11-12.
- GOVI, G. *Remarques sur les expériences de M. Thomas. Contraction du caoutchouc par la chaleur*. Les Mondes, 1869, 19, 640-2.
- GRAETZ, L. *Ueber die Abhängigkeit der Elasticität des Kautschuks von der Temperatur und ihre Beziehung zum thermischen Ausdehnungscoefficienten*. Ann. der Phys., 1886, 28, 354-64.
- GRANTHAM, J. *The Nitrogen Content of Rubber and its Relation to the Rate of Vulcanization*. Agric. Bull. F.M.S., 1915, 4, 1-4.
- . *Some Johore Soils*. Agric. Bull. F.M.S., 1916, 4, 114-121.
- . *Some Soils from the Kuala Pilah and Jelebu Districts*. Agric. Bull. F.M.S., 1916, 4, 243-7.
- . *Soils of the Sabak District on the Bernam River*. Agric. Bull. F.M.S., 1916, 4, 298-300.
- AND KNAPP, M.D. *Field Experimentation with Hevea brasiliensis*. Archief, 1918, 2, 614-30.
- GREEN, J. R. *Proteid Substances in Latex*. Proc. Roy. Soc., 1886, 40, 28-39.
- GROOM, P. *On the Function of Laticiferous Tubes*. Ann. Bot., 1889, 3, 157-168.
- GROSSANT. *Sur les moyens de faire des instruments de gomme élastique avec les bouteilles qui nous viennent du Brésil*. Ann. de chim., 1791, 11, 143-55.
- GRUNMACH, L. *Versuche über die Diffusion von Kohlensäure durch Kautschuk*. Physik. Zeit., 1905, 6, 795-800.
- HABERLANDT, G. *Zur physiologischen Anatomie der Milchröhren*. Sitzungsber. Wien, 1883, 87 Ab. I, 51-66.
- HANCOCK, T. *Personal Narrative of the Origin and Progress of the Caoutchouc or India-rubber Manufacture in England*. London, 1857. 283 pp.
- HARRIES, C. *Ueber das Verhalten des Kautschuks gegen salpetrige Säure*, Ber., 1901, 34, 2991-2.
- . *Zur Chemie des Parakautschuks*. Ber., 1902, 35, 3256-66, 4429-31.
- . *Zur Kenntnis der Kautschukarten*. Ber., 1903, 36, 1937-41.
- . *Untersuchung von latexarten in Sicilien*. Ber., 1904, 37, 3842-8.

- HARRIES, C. *Ueber den Abbau des Parakautschuks vermittelt Ozon.* Ber., 1904, **37**, 2708-11.
- . *Ueber den Weber'schen Diniro-kautschuk.* Ber., 1904, **38**, 87-90.
- . *Ueber Abbau und Konstitution des Parakautschuks.* Ber., 1905, **38**, 1195-1203.
- . *Zur Kenntnis der Einwirkung des Stickstofftrioxyds auf Kautschuk.* Zeit. angew. Chem., 1907, **20**, 1969-70.
- . *Constitution of Caoutchouc and Allied Compounds.* (Abstrs. Chem. Soc., 1915, i, 277-9.) (Original: *Annalen*, 1914, **406**, 173-226.)
- . *Chemical Investigations of the Vulcanization of Rubber and the Possibility of its Regeneration from the Vulcanized Product.* (J. Soc. Chem. Ind., 1916, **35**, 747; Chem. Abstrs., 1917, 307. Original: Ber., 1916, **49**, 1196-1201.)
- . *Untersuchungen über die natürlichen und künstlichen Kautschukarten.* Berlin, 1919. 258 pp. (Springer.)
- AND FONROBERT, E. *The Vulcanization of Caoutchouc and the Possibility of its Regeneration from Vulcanizates.* (Abstrs. Chem. Soc., 1916, i, 733. Original: Ber., 1916, **49**, 1390-8.)
- HARTJENS, J. C. *Monsternamen uit den latexmengbak in verband met het brengen op standaardgehalte.* Archief, 1917, **1**, 367-74. (Determination of the Rubber-content of Latex in the Mixing-tank for bringing to a Standard Dilution. Ibid., 374.)
- . *De invloed van verdunningswater op de latex met het oog op voortijdige coagulatie bij het brengen op standaardgehalte.* Archief, 1918, **2**, 163-183. (The Influence on Latex of the Water used for Dilution, and its Bearing on Early Coagulation during Dilution. Ibid., 184-6.)
- . *De bruikbaarheid van instrumenten als Metrolac en Latexometer op rubberondernemingen.* Archief, 1918, **2**, 256-272. (On the Use of Hydrometers (Metrolac and Latexometer) on Rubber Estates. Ibid., 273-7.)
- . *Onderzoek naar de praktische bruikbaarheid van een nieuw apparaat ter bepaling van het rubber-gehalte van latex.* Archief, 1919, **3**, 77-191. (On the Use of a New Apparatus for the Determination of the Rubber-content. Ibid., 102-4.)
- . *Invloed van verschillende bereidingwijzen op "shortness" van sheetrubber.* Archief, 1919, **3**, 515-28. (Influence of Different Methods of Preparation on "shortness" in Sheet Rubber. Ibid., 529-30.)
- HAUSMANINGER, V. *Versuche über den Sloss von Kautschukcylindern.* Sitzungsber. Wien, 1883, **88** (II), 768-781.
- HEALY, L. J. D. *An Electric Desiccator for the Analysis of Rubber and other Organic Compounds.* J. Ind. Eng. Chem., 1913, **5**, 489-90.
- HEBB, T. C. *Variation of the Rigidity of Vulcanized India-rubber with Tension.* Nova Scotian Inst. of Nat. Sc., Trans., 1900, **10**, 273-286.

- HEIM AND HENRIET. *Mécanisme de la coagulation de certains latex caoutchoutifères*. Le Caoutchouc, 1913, 7422-3.
- HEINZERLING, C. *Wertbestimmung von Kautschukwaren*. Bair. Industrie- und Gewerbeblatt, 1892, 24, 449-50. (Chem. Zentralbl., 1892, 4 (2), 762-3.)
- HEINZERLING, C. AND PAHL, W. *Investigations on the Favourable or Injurious Influence of the usual Admixtures to India-rubber and Gutta-percha upon the Technical uses of these Substances*. (Proc. Inst. Civ. Eng., 1892-3, 111 (1), 505-7; J. Soc. Chem. Ind., 1893, 12, 51-2. Original: Mitt. d. Vereins zur Beförderung des Gewerbsfleisses, 1891, 370 et seq.)
- HELBRONNER, A. AND BERNSTEIN, G. *Contribution to the Study of Rubber Solutions Vulcanized by the Ultra-violet Rays*. Rubber Industry, 1914, 156-63.
- HELLENDORF, H. J. *Over den invloed van verschillende oplosmiddelen op de viscositeit van rubberoplossingen*. Meded. Delft, 1916, 470-2.
- . *Over het ontstaan van rustiness bij sheet-rubber*. Archief, 1919, 3, 419-30. (On the Cause of Rustiness in Sheet Rubber. Ibid., 431-6.)
- HENRI, V. *Étude de la coagulation du latex de caoutchouc*. Soc. de Biol. de Paris, April 13, 1906. (Bot. Centralbl., 1907, 104, 202.)
- . *Coagulation du latex de caoutchouc et propriétés élastiques du caoutchouc pur*. C.R., 1907, 144, 431-3; Soc. franc. de Phys., 1907, No. 257, 2-3.
- . *Étude cinématographique des mouvements browniens*. C.R., 1908, 145, 1024-6.
- . *Influence du milieu sur les mouvements browniens*. C.R., 1908, 147, 62-5.
- . *Studies on the Latex of Rubber-producing Plants*. Lects. on Rubber, 1908, 203-6.
- HENRIQUES, R. *Beiträge zur analytischen Untersuchung von Kautschukwaren*. Chem.-Ztg., 1892, 16, 1595-6, 1623-6, 1644-5; 1893, 17, 707-9; 1894, 18, 411-2, 442-4, 905-6; Zeit. angew. Chem., 1899, 802-4.
- . *Ueber die Vulkanisation des Kautschuks*. Chem.-Ztg., 1894, 18, 701-2, 1155-7.
- . *Beiträge zur Kenntnis des Kautschuks*. Chem.-Ztg., 1895, 19, 235, 382-4, 403-6, 1918-20, 2043-4.
- . *Ueber die Wertbestimmung von Rohkautschuken und Kautschukwaren*. Z.f. öffentl. Ch., 1897, 3, 37-40. (Chem. Zentralbl., 1897, 1, 623.)
- HERBST, E. *Ueber die Einwirkung des atmosphärischen Sauerstoffs auf den Parakautschuk*. Ber., 1906, 39, 523-5.
- HERISSANT AND MACQUER. *Observation chimique [Solutions of Rubber]*. Histoire de l'Académie Royale des Sciences, 1763, 49-51.

- HESEHUS, N. *Abnormal Properties of Rubber*. J. Russ. Phys.-Chem. Soc., 1883, 15 (2), 103-6 (J. de Physique, 1884, 3 (2), 459-60).
- VAN HEURN, F. C. *De invloed van de bewerking op de mengwalsen op de Samenstelling en de Eigenschappen van rubber*. Meded. Delft, 1916, 376-96.
- *Kan uit eene rubber met een laag viscositeitgetal door langer vulcaniseeren een even goed product verkregen worden als uit eene rubber met een hooger viscositeitgetal?* Meded. Delft, 1916, 397-405.
- *Over den invloed van de aanwezigheid van hars op de vulcaniseerbaarheid van rubber*. Meded. Delft, 1916, 406-10.
- *Het ondervulcaniseeren van rubber*. Meded. Delft, 1916, 411-7.
- *Over de hoeveelheid zwavel, welke maximal door rubber gebonden kan worden*. Meded. Delft, 1916, 418-9.
- *Eenige waarnemingen over koude vulcanisatie*. Meded. Delft, 1916, 420.
- *Over het verbeteren van rubber door verhitting in eene Koolzuur atmosfeer*. Meded. Delft, 1916, 423-8.
- *Drukproeven met cylinders van gevulcaniseerde rubber*. Meded. Delft, 1916, 429-33.
- *Enkele waarnemingen in verband met de opzwellbaarheid van ruwe en van gevulcaniseerde rubber*. Meded. Delft, 442-5.
- *Enkele physische proeven met rubber*. Meded. Delft, 1916, 450-4.
- *Proeven betreffende den polymerisatiegraad van in latex aanwezige rubber*. Meded. Delft, 1916, 446-9.
- *Verschillende onderzoeken over de viscositeit van ruwe rubberoplossingen*. Meded. Delft, 1916, 357-75.
- *Het material der crêpewalsen*. Archief, 1918, 2, 1-6. (*The Material of the Crêpe Rollers*. Ibid., 7-11.)
- *Onderzoek van natriumbisulphat op het Algemeen Proefstation der A.V.R.O.S.* Archief, 1918, 2, 12-16. (*The Testing of Sodium Bisulphate in the Laboratory of the A.V.R.O.S.*, Ibid., 17-21.)
- *Het vochtgehalte en het droogen van ruwe rubber*. Archief, 1918, 2, 22-44. (*The Moisture-content and the Drying of Crude Rubber*. Ibid., 115-126.)
- *Natrium sulfiet analyses*. Archief, 1919, 3, 7-11. (*Sodium Sulphite Analyses*, Ibid., 12-16.)
- HILLEN, G. H. *Ueber Kautschuk- und Gutta-percha-Harze*. Diss. Bern, 1913, p. 95; Arch. Pharm., 1913, 251, 94-121.
- HINRICHSSEN, F. W. *Beiträge zur Chemie des Kautschuks*. (a) (With W. Manasse) *Zur Tetrabromidbestimmung des Kautschuks*. (b) (With W. Manasse) *Die Ermittlungen der Füllstoffe*. (c) *Zur Bestimmung des Gesamtschwefels*. (d) (With K. Meisenburg) *Kaltvulkanisation*. (e) (With E. Stern) *Heissvulkanisation*. Chem.-Ztg., 1909, 33, 735-6, 756-7.

- HINRICHSSEN, F. W. *Zur Theorie der Vulkanisation des Kautschuks*. Koll. Zeit., 1911, 8, 245-50.
- . *Zur Kenntnis der Kaltvulkanisation*. Koll. Zeit., 1911, 8, 250-1.
- . *Theory of Vulcanization*. Rubber Industry, 1911, 306-10.
- . *Report on the Actual State of Rubber Analysis*. Proc. 6th Cong. Internat. Assocn. for testing materials, New York, 1912, XXII, 1-5.
- . *Aus der physikalischen Chemie des Kautschuks*. Zeit. f. Elektrochem., 1911, 17, 809-12.
- . *Zur Kenntnis des Systems Kautschuks-Schwefel*. Zeit. f. Elektrochem., 1912, 18, 530-2.
- AND KEMPF, R. *Zur Frage der Hydrierung des Benzols*. Ber., 1912, 45, 2106-13.
- . *Ueber die Einwirkung von Jod auf Kautschuk*. Ber., 1913, 46, 1287-91.
- AND KINDSCHER, E. *Zur Frage des Molekulargröße des Kautschuks im Latex*. Ber., 1909, 42, 4329-31; Mitt. Prüfungsamt, 1911, 29, 110-4.
- . *Zur Theorie der Kaltvulkanisation des Kautschuks*. Koll. Zeit., 1910, 6, 202-9.
- . *Ueber die Unterscheidung des Para- und Ceylonkautschuksorten*. Vorläufige Mitteilung. Chem.-Ztg., 1910, 34, 230-1.
- . *Versuche über die Entschwefelung von vulkanisiertem Kautschuk*. Koll. Zeit., 1912, 10, 146-8.
- . *Die Bromidbestimmung des Kautschuks nach Hübener*. Chem.-Ztg., 1912, 36, 217-8.
- . *Zur Frage der Entschwefelung von vulkanisiertem Kautschuk*. Koll. Zeit., 1912, 11, 38-9.
- . *Zur Theorie der Vulkanisation des Kautschuks*. Koll. Zeit., 1912, 11, 191-3.
- . *Ueber die Umsetzung des Kautschuks mit Schwefelchlorür und Schwefel*. Ber., 1913, 46, 1291-7.
- . *Theory of (cold) Vulcanization*. (J. Soc. Chem. Ind., 1916, 35, 934. Original: Mitt. Prüfungsamt, 1915, 33, 407-15.)
- AND MARCUSSEN, J. *Zur Kenntnis der Kautschukharze*. Mitt. Prüfungsamt, 1911, 29, 121-9, 450-4; Zeit. angew. Chem., 1910, 23, 49-52; 1911, 24, 725-9.
- QUENSELL, H. AND KINDSCHER, E. *Ueber die Additionsverbindungen des Kautschuks mit Halogenwasserstoffsäuren und Halogenen*. Ber., 1913, 46, 1283-7.
- AND MEMMLER, K. *Der Kautschuk und seine Prüfung*. Leipzig, 1910 (Hirzel), 263 pp.
- HÖHN, J. B. *Porosity of India-rubber Articles*. (J. Soc. Chem. Ind., 1900, 19, 545. Original: Gummi-Ztg., 1900, 14, 423.)
- HOUGE DE L'AULNOIT, A. *Réglementation de la force de pression*

- des bandes et des tubes élastiques destinés à produire l'ischémie provisoire, d'après la méthode d'Esmarck.* Les Mondes, 1877, 42, 286-9.
- HOUTE DE LANGE, W. G. TEN. *Rubberproductie-Krommen.* Archief, 1918, 2, 105-11.
- HÜBENER, G. *Untersuchungen und Untersuchungsmethode von hartvulkanisierten Gummisorten.* Chem.-Ztg., 1909, 33, 144-5, 155-7.
- *Ueber hartvulkanisierten Kautschuk. I. Einfache Verfahren zur Bestimmung des Vulkanisationsschwefels in heissvulkanisierten Gummiwaren.* Gummi-Ztg., 1909, 24, 213-4.
- *Ueber hartvulkanisierten Kautschuk. III. Beitrag zur Aufklärung der Vulkanisationsvorgänge.* Gummi-Ztg., 1910, 24, 627-9.
- *Ueber die Oxydation von Kautschuk.* Gummi-Ztg., 1913, 28, 237-9.
- HÜFNER, G. *Einige Versuche über die Absorption von Gasen durch grauen vulkanisierten Kautschuk.* Ann. der Phys., 1888, 34, 1-10.
- HUTIN, A. *Extraction of Rubber, etc., with Acetone.* (J. Soc. Chem. Ind., 1915, 34, 1105. Original: Ann. Chim. anal., 1915, 20, 212-3.)
- *Estimation of Total Sulphur in Rubber Materials.* (J. Soc. Chem. Ind., 1915, 34, 1105. Original: Ann. Chim. anal., 1915, 20, 214-6.)
- *Accélérateur de vulcanisation.* Le Caoutchouc, 1918, 9596-8.
- INGLE, H. *Some Observations on Rubber Resins.* J. Soc. Chem. Ind., 1912, 31, 272-3.
- VAN ITERSOM, G. *Poreusiteit van ge vulcaniseerde rubber.* Meded. Delft, 1916, 126-42. (*Porosity of Vulcanized Rubber.* Delft Communics., Part VII, 223-37.)
- *Opmerkingen over het wezen van het vulcanisatie-proces.* Meded. Delft, 1916, 155-79. (*Remarks on the Nature of the Vulcanization Process.* Delft Communics., 239-61.)
- *Een apparat ter bepaling van het rubbergehalte van latex.* Meded. Delft, 1916, 143-54.
- *Remarks on Scientific Rubber Research, and its Importance for the Prospects of Plantation Rubber.* Rubber Recueil, 1914, 401-10. (In Dutch: Meded. Delft, 1916, 202-13.)
- , VAN HEURN, F. C. AND VAN ROSSEM, A. *Vereenvoudigde Methoden voor keuring van ruwe rubber.* Meded. Delft, 1916, 180-201.
- AND VAN ROSSEM, A. *Inleidende verhandeling tot de technisch-wetenschappelijke onderzoekingen verricht in den Rijksvoorlichtingsdienst.* Meded. Delft, 1916, 18-125. (Based on this: Delft Communics. 1917. 261 pp.)

- JOHNSON, E. H. AND UPTON, H. S. *A Volumetric Method for the Determination of Free Sulphur*. Rubber Age, 1917, 2, 11. (Chem. Abstrs., 1917, 3468.)
- JOHNSON, W. *Ueber Verarbeitung des Kautschuks*. Le Technologiste, 1853, 136. (Chem. Zentralbl., 1854, 448.)
- JONES, H. W. *On the use of Nitric Acid as a Solvent for Compounded and Vulcanized Rubbers*. Rubber Industry, 1914, 189-90.
- . *A Simple Method for the Estimation of Mineral Matters in Vulcanized Rubbers*. Rubber Industry, 1914, 199-204.
- DE JONG, A. W. K. *La presence de la Québrachite dans le latex de l'Hevea brasiliensis*. Rec. trav. chim., 1906, 25, 48-9.
- . *La presence de la Diméthylinosite inaktive dans le latex de "Melaboeabi" de Sumatra*. Rec. trav. chim., 1908, 27, 257-9.
- . *Tapproeven met Hevea*. (Tapping Experiments with Hevea.) Rubber Recueil, 1914, 311-9.
- . *Tapping and Tapping Systems for Hevea brasiliensis*. Rep. Batavia, 1914, 151-5.
- . *Wetenschappelijke tapproeven bij Hevea brasiliensis*. Meded. XIV van het Agricultuur-chemisch Laboratorium. (Archief, 1917, 1, 53-5.)
- . *Tapresultaten bij Hevea brasiliensis*. (Verzamel referaat) Archief, 1917, 1, 378-97. (Results of Tapping Experiments with Hevea brasiliensis. Summary. Ibid., 398-402.)
- . *Tapproeven bij Hevea brasiliensis*. Archief, 1918, 2, 152-5. (Tapping Experiments with Hevea brasiliensis. Ibid., 159.)
- . *Links ten opzichte van rechts tappen*. Archief, 1918, 2, 325-6. (Tapping from Left to Right versus from Right to Left. Ibid., 327.)
- . *Tapproeven bij Hevea brasiliensis*. Archief, 1919, 3, 1-5, 277-8. (Tapping Experiments on Hevea brasiliensis. Ibid., 6, 278.)
- AND TROMP DE HAAS, W. R. *Die Milch des Castilloa elastica*. Ber., 1904, 37, 3298-3301.
- . *Ueber die Ursache der Coagulation des Milchsafes von Castilloa*. Ber., 1904, 37, 3301-5.
- JOULE, J. P. *On the Thermo-Chemistry of Ferruginous Metals, and on the Thermal Effects of Stretching Solid Bodies*. Proc. Roy. Soc., 1857, VIII, 355; Phil. Mag., 1857, 14 (4), 226-7; Joule's Scientific papers, I, 405-7.
- . *On some Thermo-Dynamic Properties of Solids*. Phil. Trans., 1859, 149, 91-131; Joule's Scientific Papers, I, 413-73.
- KAHLENBERG, L. *Note on the Phenomena of Osmosis and Osmotic Pressure in Observations Relative to Dialysis*. J. Phys. Chem., 1906, 10, 141-209.



- KASSNER, G. *Determination of Caoutchouc in Plants*. (Chem. News, 1889, 59, 109. Original: Arch. Pharm.)
- KAWAKANI, K. *Depolymerization of Raw Rubber*. Kogyo-Kwagaku-Zasshi, 1918, 21, 226-31. (J. Soc. Chem. Ind., 1918, 37, 476 A).
- KAYE, F. *The Chemical Coagulation of Rubber Latex*. Rubber Industry, 1914, 137-43.
- KAYSER, H. *Ueber Diffusion und Absorption durch Kautschuk*. Ann. der Phys. 1891, 48, 544-53.
- KELSEY, C. A. *Electrical Requirements of Certain Machines in the Rubber Industry*. Proc. Amer. Inst. Elec. Eng., 1913, 32, 1598-1604.
- KERBOSCH, M. *Sur le présence de l'aldehyde acétique et de l'acide prussique dans le latex d'Hevea brasiliensis*. Rubber Recueil, 1914, 361-3; Rec. trav. chim., 1915, 24, 235-8.
- . *Bepaling van het Rubbergehalte van Hevea latex. Acetaldehyde en Blauwzuur in Hevea latex. Proeven over Oxydeerbaarheid van Hevea rubber*. Meded. over Rubber, No. III, 1914. 44 pp.
- KEUCHENIUS, P. E. *Gegevens over den diktegroei van Hevea*. Archief, 1918, 1, 407-30. (The Increase in Girth of Hevea Trees. Ibid., 431-2.)
- KING, A. H. *Rubber Vulcanization Accelerators*. Chem. Met. Eng., 1916, 15, 231-4.
- KIRCHHOF, F. *Ueber die Oxydation von Kautschuk*. Koll. Zeit., 1913, 13, 49-61.
- . *Ueber die Oxydation des Kautschuks*. Gummi-Ztg., 1913, 28, 414-5.
- . *Zur Kenntnis der Additionsreaktion des Kautschuks. Ein Beitrag zu dessen Konstitutionsaufklärung, sowie Versuch einer Theorie der Vulkanisation*. Koll. Zeit., 1914, 14, 35-43.
- . *Ueber den Einfluss des Lösungsmittel auf die Viscosität von Kautschuklösungen*. Koll. Zeit., 1914, 15, 30-36.
- . *The Swelling of Vulcanized Rubber*. (Chem. Abstrs., 1915, 1134; J. Soc. Chem. Ind., 1914, 838. Original: Kolloidchem. Beih., 1914, 6, 1-22.)
- . *The Regeneration of Caoutchouc from its Tetrabromide*. (Chem. Abstrs., 1915, 871; J. Soc. Chem. Ind., 1915, 500. Original: Koll. Zeit., 1914, 15, 126-31.)
- KISSLING, R. *Zur Prüfungstechnischer Kautschukwaren*. Chemischen Industrie, 1888, 11, 217; Dingler's Polyt., 1888, 270, 376-81.
- KLEIN, O. H., LINK, J. H. AND GOTTSCH, F. *The Aniline Method for Determination of Fillers in Rubber Goods*. J. Ind. Eng. Chem., 1917, 9, 140-1.
- KNIEP, H. *Ueber die Bedeutung des Milchsafte der Pflanzen*. Flora, 1905, 94, 129 et seq.
- . *Die Funktion des Milchsafte*. Rubber Recueil, 1914, 63-92.

- KOBBE, F. *Ueber das Diffusionsvermögen der Kohlensäure in Bezug auf Kautschuk*. Chem. Zentralbl., 1890, 617.
- KOHLRAUSCH, F. *Notiz über die Wärme-Ausdehnung des Hartgummi*. Ann. der Phys., 1873, 149, 577-9; Dingler's Polyt., 210, 445-6.
- . *Bemerkungen zu Hrn. Neesen's Beobachtungen über die elastischen Nachwirkung*. Ann. der Phys., 1875, 155, 579-87.
- . *Experimental-Untersuchungen über die elastische Nachwirkung bei der Torsion, Ausdehnung und Biegung*. Ann. der Phys., 1876, 158, 337-75.
- KOKETSU, R. *Studien über die Milchröhren und Milchzellen einiger einheimischer Pflanzen*. Bot. Mag. Tokyo, 1913, 27, 133; J. Coll. Sc. Tokyo, 1913-5, 35, Article 6, 57 pp.
- KONINGH, L. DE. *Estimation of Mineral Matter in Rubber Goods*. J. Amer. Chem. Soc., 1897, 19, 952-6.
- KORNECK, O. *Kritische Untersuchungen über die analytischen Bestimmungsmethoden des Kautschuks*. Gummi-Ztg., 1910, 25, 4, 42, 78.
- KORTEWEG, D. J. AND JULIUS, V. A. *Ueber das Grössenverhältniss der elektrischen Ausdehnung bei Glas und Kautschuk*. Sitzungsber. Wien, 1881, 83 (II), 29-36; Ann. der Phys., 1881, 12, 647-54.
- KRATZ, G. D. *Rate of Vulcanization and Factory Output*. I. R. Review, 1916, 16, 225-7; I. R. J., 1916, 51, 661-2.
- AND FLOWER, A. W. *The Vulcanization of Rubber at a Constant Temperature, and by a Series of Increasing Temperatures*. J. Ind. Eng. Chem., 1919, 11, 30-3.
- . *Effect of Certain Accelerators on the Properties of Vulcanized Rubber*. Chem. Met. Eng., 1919, 20, 417-20.
- KRATZ, G. D., FLOWER, A. H., AND COOLIDGE, C. *The Action of certain Organic Accelerators in the Vulcanization of Rubber*. Jour. Ind. Eng. Chem., 1920, 12, 317-24.
- KRAYENHOFF VAN DE LEUR, G. C. *Over het opnemen van vocht door ruwe rubber in lucht van verschillend vochtgehalte*. Meded. Delft, 1916, 473-9.
- KUNDT, A. *Temporärer Dichroismus, hervorgebracht durch Zug*. Ann. der Phys., 1874, 151, 125-6.
- KURZ, A. *Der Elasticitätsmodul des Kautschuk*. Repertorium, 1887, 23, 311-12.
- LAMPE, A. *Zur Molekulartheorie anisotroper Dielektrica mit einer experimentellen Bestimmung der Dielektricitätskonstante einer gespannten Kautschukplatte senkrecht zur Spannungsrichtung*. Sitzungsber. Wien, 1902, 111 (II Ab.), 982-95.
- LANG, V. V. *Ueber transversale Töne von Kautschukfäden*. Sitzungsber. Wien, 1898, 107 (II Ab.), 692; Ann. der Phys., 1899, 68, 335-42.
- M M

- LEBEDEFF, J. *The Thermal Expansion of Rubber*. J. Russ. Phys.-Chem. Soc., 1881, **13** (2), 246-58. (Chem. Zentralbl., 1882, **13**, 17.)
- LEDERER, A. *Die Viscosität von Kautschuklösungen als Wertbestimmung für Kautschuksorten*. Jahrb. der Kaut. Ind., Literaische Beilage zum Gummikalender, 1912, 146.
- LEROUX. *Température du caoutchouc dilaté*. Cosmos, 1857, XI, 657-6. (Fortschr. Phys., 1857, 292.)
- LEWIS, E. W. AND WAUMSLEY, H. *India-rubber as a Protective Colloid. Formation of Colloidal Metallic Sulphides in Rubber Solutions*. J. Soc. Chem. Ind., 1912, **31**, 518-20; Koll. Zeit., 1912, **11**, 39-41.
- LINET, L. *Les recherches de M. Aimé Girard sur les laites de caoutchouc*. Bull. Soc. Chim., 1898, **19** (3), 812-15.
- LOBRY DE BRUYN, C. A. *Untersuchung von Kautschukgegenständen*. Chem.-Ztg., 1894, **18**, 309-12, 329-30, 1566, 1618.
- LOCK, R. H. *Rubber and Rubber Planting*. Cambridge, 1913. 245 pp.
- . *Notes on the Physiology of the Latex Production in Hevea*. Rubber Industry, 1914, 114-23.
- AND BAMBER, M. K. *Hevea. Heneratgoda Experiments, 1911-2*. Dept. Agric. Ceylon, Bull. No. 1, 1912.
- LOEWEN, H. *Zur Theorie der Vulkanisation des Kautschuks*. Zeit. angew. Chem., 1912, **25**, 1553-60, 1610-2.
- . *Bemerkungen zur Vulkanisation des Kautschuks*. Gummi-Ztg., 1913, **27**, 744.
- . *Ueber die Löslichkeit von Schwefel in Kautschuk*. Gummi-Ztg., 1913, **27**, 1301-2.
- LUNDAL, A. E. *Beiträge zur Kenntniss der physikalischen Eigenschaften des Kautschuks*. Ann. der Phys., 1898, **66**, 741-59.
- MAAS, J. G. J. A. *Betrouwbaarheid van veldproeven bij Hevea*. Archief, 1918, **2**, 561-607. (Reliability of Field Experiments with Hevea. Ibid., 608-13.)
- MACDONALD, W. A. *Note on the Variation with Tension of the Elastic Properties of Vulcanized India-rubber*. Nova Scotia Inst. Nat. Sc., Proc. 1898-9, **10**, xxviii-xxxiv.
- MACLAREN, W. DE BOIS. *The Rubber-Tree Book*. London, 1913.
- MACQUER. *Sur la dissolution du caoutchouc ou résine élastique de Cayenne*. Hist. de l'Académie des Sc., 1768, 58-61.
- . *Sur un moyen de dissoudre la résine caoutchouc, comme présentement sous le nom de résine élastique de Cayenne, et de la faire reparoître avec toutes ses qualités*. Mémoires de l'Académie Royale des Sciences, 1768, 209-17.
- MADAN, H. G. *On the Behaviour of Stretched India-rubber when Heated*. Nature, 1885, **32**, 625.
- MALET, A. H. *Rubber Seed Selection*. Agric. Bull. F.M.S., 1917, **5**, 271-4.

- MALLOCK, A. *The Physical Properties of Vulcanized India-rubber.* Proc. Roy. Soc., 1889, 46, 233-49.
- MAQUENNE, L. *Recherches sur la Dambonite et la Dambose.* Ann. de Chim. Phys., 1887, 12 (6), 566-74.
- . *Sur l'identité du dambose et de l'inosite.* C.R., 1887, 104, 1853-5.
- MARQUIS, R. AND HEIM, F. *Sur une methode de dosage du caoutchouc pur dans le caoutchouc brut.* Bull. Soc. Chim., 1913, 13 (4), 862-6.
- MARTIN, W. G. *The Effect of Acids and Alkalies on Rubber, more especially in Relation to Reclaimed Rubber.* Rubber Industry, 1914, 205-11.
- MAYER, O. *Ein Beitrag zur Analyse von Kautschukwaren.* Chem.-Ztg., 1902, 26, 481.
- MEMMLER, K. *Mechanical Tests for Rubber.* Rubber Industry, 1911, 351-73.
- . *The Present Condition of the Mechanical Testing of India-rubber according to the Experience gained from the Experiments conducted at the Royal Laboratory for Testing Materials, Berlin-Lichterfelde W.* Proc. 6th Cong. Internat. Assocn. for testing materials, New York, 1912, XXII. 8 pp.
- AND SCHOB, A. *Beiträge zur Frage der mechanischen Prüfung von Weichgummi.* I. Ueber den Einfluss der Probenform auf die Festigkeitsergebnisse. II. Ueber den allgemeinen Charakter der mechanischen Weichgummiprüfung und über einige Eigentümlichkeiten der ringförmigen Probe. III. Abnutzungsversuche. IV. Prüfung zweier Automobilvollgummireifen. Mitt. Prüfungsamt, 1909, 27, 173-238; 1911, 29, 185-211; 1912, 30, 139-49; 1913, 31, 437-51.
- MILLER, W. A. *On the Decay of Gutta-percha and Caoutchouc.* Jour. Chem. Soc., 1865, 18, 273-84.
- MILLS, H. P. *A Punch for Straight Rubber Test Pieces.* J. Ind. Eng. Chem., 1912, 4, 452.
- MINIKES, S. *Apparat zur schneller Bestimmung der Spezifischen Gewichtes von Kautschuk und verwandten Stoffen.* Chem. Zentralbl., 1899, I, 578.
- MOHR, E. C. *On Rubber Soils.* Rubber Recueil, 1914, 167-70.
- MORGAN, S. *The Preparation of Plantation Para Rubber.* London, 1913. 269 pp.
- . *Recommendations for the Treatment of Latex and Rubber.* I.R.J., 1915, 49, 292-3.
- NACCARI AND BELLATI. *Sul rapporto fra l'accorciamento unitario delle dimensioni trasversali di un' asta di caucciù striata e l'allungamento unitario in senso longitudinale.* Cimento, 1877, 2 (3), 217-40. (Fortschr. Phys., 1878, 213; Beibl. Phys., 2, 580-1.)
- NEESEN. *Ueber elastische Nachwirkung bei Torsion.* Monatsber. K. Preuss. Akad. Wiss., 1874, 141-8.

- NEESEN. *Beitrag zur Kenntniss der elastische Nachwirkung bei Torsion.* Ann. der Phys., 1874, **153**, 498-524.
- OBACH, E. *Durchlässigkeit des Kautschuks für Kohlensäure.* Chem.-Ztg., **14**, 1142.
- OLSEN, T. J. *An Autographic Rubber-Testing Machine.* Proc. Amer. Soc. for testing materials, 1910, **10**, 588-91.
- ONO, S. *Elongation of India-rubber.* Phys. Soc., Tokyo, Proc., 1913, **7**, 36-43. (Sc. abstrs., 1913, A, 451.)
- OOSTING, H. J. *Phaseverschillen bij gedwongen transversale en longitudinale trillingen van gespannen caoutchoucdraden.* Versl. K. Ak. van Wet., 1895, **3**, 262-6. (Fortschr. Phys., 1895, **1**, 425; Beibl. Phys., **19**, 539.) (Beibl. Phys., **18**, 709.)
- *Stroboskopisch onderzoek en intermitterende photographie bij gedwongen trillingen van gespannen caoutchoucdraden.* Versl. K. Ak. van Wet., 1895, **4**, 152-4. (Fortschr. Phys., 1895, **1**, 425; Beibl. Phys., **20**, 545.)
- OSTROMYSLENSKY, I. I. *New Method for the Vulcanization of Caoutchouc by means of Trinitrobenzene or Benzoyl Peroxide.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1885-92. (J. Soc. Chem. Ind., 1916, **35**, 369; Abstrs. Chem. Soc., 1916, **1**, 276-7; Chem. Abstrs., 1916, 1943-4.)
- *Mechanism of the Action of Amines and Metallic Oxides on the Vulcanization of Caoutchouc.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1892-8.
- *New Method for the Vulcanization of Caoutchouc by means of Halogenated Compounds. Mechanism of Vulcanization.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1898-1904.
- *New Method of Vulcanization by means of Molecular Oxygen, Ozone, or Ozonides of Organic Compounds.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1904-9.
- *Mechanism of the Process of Vulcanization of Caoutchoucs.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1453-61. (J. Soc. Chem. Ind., 1916, **35**, 59; Chem. Abstrs., 1916, 3177; I.R.J., 1916, **52**, 467-9.)
- *Hot Vulcanization of Caoutchouc by Nitro Compounds, without Sulphur.* J. Russ. Phys.-Chem. Soc., 1915, **47**, 1462-7. (J. Soc. Chem. Ind., 1916, **35**, 59; Chem. Abstrs., 1916, 3177; I.R.J., 1916, **52**, 469-70.)
- *Hot Vulcanization of Caoutchoucs by Peroxides or Peracids, without Sulphur.* J. Russ. Phys.-Chem. Soc., 1915, 1467-71. (J. Soc. Chem. Ind., 1916, **35**, 59; Chem. Abstrs., 1916, 3177-8; I.R.J., 1916, **52**, 470-2.)
- OSTWALD, WO. *Beiträge zur Kolloidchemie des Kautschuks.* I. Zur Theorie der Vulkanisation. II. Weitere Bemerkungen zur Theorie der Kaltvulkanisation. Koll. Zeit., 1910, **6**, 136-55, **7**, 45-9.
- *Bemerkungen zu der Arbeit von Spence und Young.* Koll. Zeit., 1912, **11**, 34-6.

- PAGE, C. G. *Singular Property of Caoutchouc, Illustrating the Value of Latent Heat in giving Elasticity to Solid Bodies, etc.* Amer. Jour. Sc. and Arts (Sillman), 1847, 4 (2), 341-2.
- PARKIN, J. *Observations on Latex and its Functions.* Ann. Bot., 1900, 14, 197-214.
- . *The Science and Practice of Para-rubber Cultivation.* Sc. Progress, 1909-10, 4, 393, 593.
- PAYEN, M. *Mémoire sur le caoutchouc et le gutta-percha.* C.R., 1852, 34, 2-8.
- . *Extrait d'un mémoire sur la sulfuration du caoutchouc et sur quelques propriétés du soufre.* C.R., 1852, 34, 453-9.
- . *Sur la porosité du caoutchouc relativement à la dialyse des gaz.* C.R., 1866, 63, 533-7.
- PEACHEY, S. J. *The Action of Gaseous Oxygen on India-rubber.* J. Soc. Chem. Ind., 1912, 31, 1103-5; 1913, 32, 179-80.
- . *Vulcanization Accelerators.* J. Soc. Chem. Ind., 1917, 36, 326, 424-9, 950; J. Munic. Sch. Tech. Mchstr., 1916, 8, 181-4.
- AND LEON, M. *The Oxidation of Rubber.* J. Soc. Chem. Ind., 1918, 37, 55-60.
- PERROT, E. *Le rôle du caoutchouc chez l'Hevea et les autres plantes à caoutchouc.* Le Caoutchouc, 1914, 11, 8019-23.
- PETCH, T. *The Physiology and Diseases of Hevea brasiliensis.* London, 1911. 268 pp. (Dulau.)
- . *Hevea Tapping Results.* Dept. Agric. Ceylon, Bulls. Nos. 12, 13 (1914), 17, 20 (1915), 25 (1916), 34 (1917).
- PEYRON. *Note sur la propriété qu'a le caoutchouc de laisser passer les gaz.* C.R., 1841, 13, 829-4.
- PHILLIPS, P. *The Slow Stretch in India-rubber, Glass, and Metal Wires when Subjected to a Constant Pull.* Phil. Mag., 1905, 9 (6), 513-31.
- PICKLES, S. S. AND HAYWORTH, W. P. *Composition of Para Rubber-Seed Oil.* Analyst, 1911, 36, 491-2.
- AND WHITFIELD, B. W. *The Carbohydrate Constituents of Para Rubber.* Proc. Chem. Soc., 1911, 27, 54.
- PONTIO, M. *Analyse du caoutchouc et de la Gutta-percha.* Paris.
- . *A Direct Method of Determining Pure Caoutchouc in Raw Rubber.* (Chem. Zentralbl., 1914, I, 303. Original: Rev. gen. de chim. pure et appl., 1913, 16, 400-1.)
- . *The Direct Determination of Caoutchouc in Raw Rubber according to Marquis and Heim.* (Chem. Zentralbl., 1914, I, 2070. Original: Ann. chim. anal. appl., 19, 60-2.)
- PORRITT, B. D. *The Chemistry of Rubber.* London, 1913. 93 pp.
- . *The Rubber Industry—Past and Present.* J. Soc. Arts, 1919; I.R.J., 1919, 57, 411-15, 445-8, 489-91.
- AND WHEATLEY, R. *Experiments on the Determination of Mineral Matter in Rubber Mixings.* Rubber Industry, 1914, 193-9.

- POTTS, H. E. *The Oxidation of Sulphur by Nitric Acid*. Rubber Industry, 1911, 336-43.
- . *The Chemistry of the Rubber Industry*. London, 1912. (Constable.)
- POSNJAK. *Ueber den Quellungsdruck*. Koloidchem. Beih., 1912, 3, 417-56.
- POYNTING, J. H. *The Changes in the Length and Volume of an India-rubber Cord when Twisted*. I.R.J., 46, 262.
- PULFRICH, C. *Photometrische Untersuchungen über Absorption des Lichtes in isotropen und anisotropen Medien*. Ann. der Phys., 1881, 14, 177-218.
- . *Ueber die elastische Nachwirkung eines Kautschukschlauches und deren Einfluss auf die Constante*. Ann. der Phys., 1886, 28, 87-107.
- PUSCHL, C. *Ueber die Volumenveränderung des Kautschuks durch Wärme*. Repertorium, 1875, 11, 102-5; Sitzungsber. Wien, 1875, 71 II Ab., 95-9.
- . *Ueber den Einfluss von Druck und Zug auf die thermischen Ausdehnungscoefficienten der Körper und über das bezüglichliche Verhalten von Wasser und Kautschuk*. Wien Anz., 1875, 144. (Chem. Zentralbl., 1875, 561; J. Chem. Soc., 1876, ii, 41).
- . *Ueber das Verhalten des gespannten Kautschuks*. Sitzungsber. Wien, 1888, 97 II Ab., 660-4.
- QUINCKE, G. *Ueber electrische Ausdehnung*. Ann. der Phys., 1880, 10, 197-201, 401-5.
- REINHARDT, C. *Beiträge zur Untersuchung des vulkanisierten Kautschuks*. Zeit. anal. chem., 1885, 25, 267-9.
- . *Analysis of Vulcanized Caoutchouc*. (Chem. News, 1885, 52, 225.)
- REYCHLER, A. *Diffusion of some Gases through Rubber Sheets*. (Abstrs. Chem. Soc., 1893, ii, 564-5. Original: Bull. Soc. Chim., 9 (3), 404-9.)
- . *Absorption of Carbon Dioxide and Sulphur Dioxide by Rubber and Blood Charcoal*. (Abstrs. Chem. Soc., 1910, ii, 272; 1911, ii, 19. Original: J. de chim. phys., 1910, 8, 3-9, 617-29.)
- RODT, V. *Diffusion of Carbon Dioxide through Rubber*. (J. Soc. Chem. Ind., 1915, 34, 187. Original: Chem.-Ztg., 1914, 38, 1249-51.)
- RÖNTGEN, W. C. *Ueber das Verhältniss der Quercontraction zur Längendilatation bei Kautschuk*. Ann. der Phys., 1876, 159, 601-16.
- . *Mittheilung einiger Versuche aus den Gebiet der Capillarität*. Ann. der Phys., 1878, 3, 321-8.

- ROSENSTEIN, L. AND DAVIES, E. L. *The Determination of Sulphur in Rubber*. Chemist-Analyst, No. 15, Oct. 1915. (I.R.J., 1919, 57, 1100.)
- VAN ROSSEM, A. *Het pekkig worden van rubber*. Meded. Delft, 1912, 54-65. (Ueber das Leimigwerden des Kautschuks. Koll. Zeit., 1913, 12, 78-83.)
- *On the Depolymerization of Raw Rubber*. Rubber Industry, 1914, 149-55. (Also in Dutch: Meded. Delft, 1916, 465-9.)
- *Bijdrage tot de kennis van het Vulcanisatieproces*. (Diss.) Amsterdam, 1916. 192 pp.
- *Trekproeven met den dynamometer van P. Breuil*. Meded. Delft, 1916, 455-64.
- ROSSI, P. *La doppia rifrazione accidentale nel caucciù studiata in rapporto al comportamento elastico*. Cimento, 1910, 20 (5), 226-37; Rend. di Napoli, 1910, 125-34. (Sc. Abstrs., 1910, A, 573; Beibl. Phys., 1911, 206-7.)
- *La doppia rifrazione accidentale e le azioni elastiche susseguenti nel caucciù*. Cimento, 1910, 20 (5), 268-77; Rend. di Napoli, 1910, 16 (3), 142-51. (Beibl. Phys., 1911, 364.)
- ROUX, LE. *Sur quelques observations concernant la porosité du caoutchouc*. C.R., 1866, 63, 917-18.
- RUSSNER, J. *Ueber die Wärmeausdehnung des Schwefels, Kautschuks, Hartgummis, der Gutta-percha und des Paraffins, sowie über die Verwendbarkeit des Hartgummis zu Compensationspendeln*. Repertorium, 1882, 18, 152-77.
- *Ueber das scheinbar abnorme Verhalten des gespannten Kautschuks und Gutta-percha*. Repertorium, 1882, 18, 206-16.
- *Ueber die Abhängigkeit der Elasticität des Kautschuks von der Temperatur*. Ann. der Phys., 1891, 43, 533-43.
- RUTGERS, A. A. L. *Tap en tapproeven op Sumatra's Oostkust*. Archief, 1918, 2, 133-147, 198-8. (Tapping and Tapping Experiments on the East Coast of Sumatra. Ibid., 148-51, 199-202.)
- *Selectie en Uildunning*. Archief, 1919, 3, 105-18 (Selection and Thinning-out. Ibid., 119-123.)
- AND MAAS, J. G. J. A. *De bruikbaarheid van latexwegers voor productiemetingen*. Archief, 1917, 1, 289-311. (Summary: Ibid., 312.)
- SAINT-VENANT, DE. *Mémoire sur l'équilibre des corps solides, dans les limites de leur élasticité, et sur les conditions de leur résistance, quand les déplacements éprouvés par leurs points ne sont pas très-petits*. C.R., 1847, 24, 260-3.
- SANDERSON, C. W. *The Expansion of Rubber Compounds during Vulcanization*. Jour. Ind. Eng. Chem., 1920, 12, 37-40.
- SCHIDROWITZ, P. *The Structure of Crude India-rubber. Preliminary note*. J. Soc. Chem. Ind., 1909, 28, 6.



- SCHIDROWITZ, P. *Die Viscosität von Kautschuk und Kautschuklösungen*. Gummi-Ztg., 1909, **23**, 703-4.
- . *Rubber*. London, 1911. 303 pp. (Methuen.)
- . *Variability*. Rubber Industry, 1914, 212-19.
- . *Our Knowledge of Coagulation and Methods of Coagulation*. Rubber Recueil, 1914, 364-73.
- . *Recent Advances in the Analysis and Evaluation of Rubber and Rubber Goods*. Analyst, 1915, **40**, 223-33.
- AND GOLDSBROUGH, H. A. *The Viscosity of India-rubber and India-rubber Solutions: with Special Reference to its Bearing on the Strength or "Nerve" of Crude Rubber*. J. Soc. Chem. Ind., 1909, **28**, 3-6.
- . *The Viscosity of India-rubber and its Solutions*. Rubber Industry, 1911, 260-4.
- . *Die Bestimmung des Viscositätsgrades von Kautschuklösungen*. Koll. Zeit., 1913, **13**, 46-9.
- . *The Relationship of Mechanical to Chemical Properties of Vulcanized Rubber*. I.R.J., 1915, **51**, 505.
- . *The Stability of Vulcanized Rubber and the "Optimum" Cure*. I.R.J., 1916, **52**, 615-20.
- . *Vulcanization Results obtained with Rubbers from Seven Plantations*. I.R.J., 1917, **54**, 162-7, 184-7.
- . *The Coefficient of Vulcanization and the State of Cure*. I.R.J., 1917, **53**, 327-8.
- . *The Rubber Stress-strain Curve*. I.R.J., 1919, **57**, 269-70.
- . *Studies in Vulcanization. A. The Rubber Stress-strain Curve*. J. Soc. Chem. Ind., 1919, **38**, 347-52 T.
- AND KAYE, F. *India-rubber from an Abnormal Latex*. (J. Soc. Chem. Ind., 1907, **26**, 935.)
- SCHIFF, P. *The Compression of Rubber Cylinders*. J. Russ. Phys.-Chem. Soc., 1881, **13**, 265.
- SCHILLER, L. *Ueber die Poissonische Konstante des Kautschuks*. Ann. der Phys., 1907, **22**, 204-8.
- . *Die Änderung der Dielektrizitätskonstante des Kautschuks bei Zug senkrecht zur Kraftlinien*. Ann. der Phys., 1911, **35** (4), 931-82.
- SCHILLER, N. *Einige experimentelle Untersuchungen über elektrische Schwingungen*. Ann. der Phys., 1874, **152**, 535-65.
- SCHIMPER, A. F. W. *Ueber Bildung und Wanderung der Kohlenhydrate in den Laubblättern*. Bot. Zeitg., 1885, **43**, 771-9.
- SCHIPPEL, H. F. *Volume Increase of Compounded Rubber under Strain*. Jour. Ind. Eng. Chem., 1920, **12**, 33-7.
- SCHMITZ, W. C. *Ueber Stickstoffbestimmung im Kautschuk*. Gummi-Ztg., 1913, **26**, 18, 877-9.
- . *Der so genannte "unlösliche" Bestandteil des Kautschuks und seine Isolierung*. Gummi-Ztg., 1913, **27**, 1085-7, 1131-3.
- . *The Isolation and Characterization of the Insoluble Constituent of Rubber*. (Chem. Abstrs., 1915, 163. Original: Gummi-Ztg., 1914, **28**, 1740.)

- SCHMITZ, W. C. *Beiträge zur Kenntnis der Konstitution des Kautschuks mittels Brom*. Gummi-Ztg., 1919, **34**, 167-9, 193-5.
- SCHMULEWITSCH, G. *Ueber den Einfluss der Wärme auf die Elasticität des Kautschuks*. Ann. der Phys., 1871, **144**, 280-7. (Bull. de l'Acad. de St. Petersbourg, 1870, **14**, 517-23; Züricher Vierteljahrsschrift, **11**, 866; Les Mondes, 1872, **27**, 354-9.)
- SCHNEEBELI, H. *Sur les déformations que subissent des sphères en caoutchouc par les forces extérieures*. Arch. Sc. Phys., 1886, **15** (3), 534-42. (Beibl. Phys., **10**, 602; Fortschr. Phys., 1886, **1**, 466.)
- SCHWARTZ, A. "Flexibles," with Notes on the Testing of Rubber. J. Inst. Elec. Eng., 1907, **39**, 31-119.
- The Testing of Rubber for Electrical Work. J. Inst. Elec. Eng., 1910, **44**, 693-752.
- AND KEMP, P. *Some Physical Properties of Rubber*. Mem. and Proc. Mchstr. Soc., 1911, **55**, No. XII; Jour. Munic. Sch. Technology, Mchstr., 1911, **4**, 221-34.
- Les phénomènes thermiques dans le caoutchouc. Le Caoutchouc, 1911, June. (Jour. Munic. Sch. Technology, Mchstr., 1912, **5**, 263-5.)
- SCHWERDTFEGGER, J. *Beiträge zur Erkennung der gewöhnlichen Auflösung des Kautschuks und zur Unterscheidung des Kautschuks und der Gutta-percha*. Neues Jahrb. f. prakt. Chem., **1**, 100-11. (Chem. Zentralbl., 1854, **25**, 214.)
- SEARLE, C. F. C. *A Method of Determining the Thermal Conductivity of India-rubber*. Proc. Cambridge Phil. Soc., 1907, **14**, 190-3.
- SEIDL, E. *Ueber die Wirkung des Bleioxyds bei der Heissvulkanisation des Kautschuks*. Gummi-Ztg., 1911, **25**, 710-13, 748-51.
- SHARPLES, A. *The Spotting of Prepared Plantation Rubber*. Dept. Agric. F.M.S., Bull. No. 19, 1914. 31 pp.
- *The Laticiferous System of Hevea brasiliensis and its Protective function*. Ann. Bot., 1918, **32**, 247-51.
- SHEDD, J. C. AND INGERSOL, R. L. *The Elastic Modulus and Elastic Limit of Rubber and their Relation to Change of Temperature*. Physical Review, 1904, **19**, 107-16.
- SHORE, A. F. *The Property of Hardness in Metals and Materials*. Proc. Amer. Soc. for testing materials, 1911, **11**, 733-9.
- SIEVERS, A. F. *Notes on the Rubber from Eucommia Ulmoides, Oliver*. Jour. Amer. Chem. Soc., 1917, **39**, 725-31.
- SIMON, E. V. *Zapversuche an Hevea brasiliensis, mit besonderer Berücksichtigung der latex produktion, der Neubildung der Rinde an den Zapstellen, sowie des Verhaltens der Reservestoffe in Stamme*. Der Tropenpflanzer, 1913, **17**, 63, 119, 181.
- SKELLON, H. *Migration of Sulphur and Vulcanization*. I.R.J., 1913, **46**, 251-2.

- SKELLON, H. *The Rôle of Polyprene Sulphide in Vulcanization.* I.R.J., 1913, **46**, 723-4.
- . *The Mass Action of Sulphur in Vulcanization.* Rubber Industry, 1914, 172-80. (Koll. Zeit., 1914, **14**, 96-105.)
- SKINNER, E. B. *The Thinning-out of Hevea Rubber Trees.* Rep. Batavia, 1914, 112-22.
- SÖHNGEN, N. L. AND FOL, J. G. *Die Zersetzung des Kautschuks durch Microben.* Centralbl. f. Bakter., 1914, **40** (2 Ab.), 87-98.
- SPENCE, D. *On the Chemical Nature of the Albanes in the Rubber from Ficus vogelii.* Jour. Inst. Comm. Res. in the Tropics, Liverpool, 1907; Ber., 1907, **40**, 999-1000.
- . *Analysis of the Latex of Funtumia elastica, Stapf.* Inst. Comm. Res. Tropics, Liverpool, 1907, Reprint No. 9.
- . *Methods of Analysis of Raw Rubber.* Inst. Comm. Res. Tropics, Liverpool, Reprint No. 10 (Chem. Zentralbl., 1908, **1**, 744).
- . *Distribution of the Protein in Para Rubber, and its Relation to Weber's Insoluble Oxygen-Addition Compound of India-rubber.* Jour. Inst. Comm. Res. in the Tropics, Liverpool, 1907, 47-60.
- . *Analysis of the Latex from Ficus Vogelii Miq. and of Memleku Rubber therefrom.* Jour. Inst. Comm. Res. in the Tropics, Liverpool, 1907, 64-75.
- . *On the Presence of Oxydases in India-rubber, with a Theory in Regard to their Function in the Latex.* Biochem. Jour., 1908, **3**, 165-81.
- . *The Presence of an Oxidizing Enzyme in the Latex of Hevea brasiliensis.* Biochem. Jour., 1908, **3**, 351-2.
- . *The Practical Significance of Recent Advances in the Bio-Chemistry of the Latex of Rubber-Producing Plants.* Lects. on Rubber, 1908, 193-9.
- . *Comparative Size of Caoutchouc Globules in the Latices of Hevea brasiliensis and Funtumia elastica.* I.R.J., 1908, **36**, 233-4.
- . *Ueber einige einleitende Versuche zur Klärung der Ursache des Leimigwerdens von Rohkautschuk.* Koll. Zeit., 1909, **4**, 70-6.
- . *Zur Bestimmung des Kautschuks als Tetrabromid.* Einfluss des Proteins. Gummi-Ztg., 1909, **24**, 212-13.
- . *Beiträge zur Chemie des Kautschuks. III. Zur Theorie der Vulkanisation II.* Koll. Zeit., 1911, **9**, 300-6.
- . *Beiträge zur Chemie des Kautschuks. IV. Einfluss niedrigen Temperaturen auf die Geschwindigkeit der Heissvulkanisation.* Koll. Zeit., 1912, **10**, 299-306.
- . *Einige Bemerkungen zur Theorie der Vulkanisation.* Koll. Zeit., 1913, **12**, 84-5.
- . *On the Relationship of Mechanical to Chemical Properties of Vulcanized Rubber.* I.R.J., 1916, **52**, 861.

- SPENCE, D. *Organic Vulcanizing Accelerators*. J. Soc. Chem. Ind., 1917, 36, 118-9.
- *Catalysts in Vulcanization*. J. Ind. Eng. Chem., 1918, 10, 115-7.
- AND GALLETTY, J. C. *On the Action of Chromyl Chloride on India-rubber*. J. Amer. Chem. Soc., 1911, 33, 190-4.
- AND SCOTT, J. H. *Zur Bestimmung des Kautschuks als Tetrabromid. Zersetzung des Bromid durch Salpetersäure*. Gummi-Ztg., 1911, 25, 301-3.
- AND KRATZ, G. D. *Ueber die unlöslichen Bestandteile des Rohkautschuks, deren Isolation und Charakterisierung*. Koll. Zeit., 1914, 14, 262-77.
- *The Swelling of Rubber in Organic Liquids*. (Abstrs. Chem. Soc., 1915, 1, 280; Chem. Abstrs., 1915, 980. Original: Koll. Zeit., 1914, 15, 217-26.
- AND SCOTT, J. H. *Beitrag zur Chemie des Kautschuks. Theorie der Vulkanisation*. Koll. Zeit., 1911, 8, 304-12.
- *Beiträge zur Chemie des Kautschuks. II. Physico-chemische Untersuchung der Harzextraktion*. Koll. Zeit., 1911, 9, 83-5.
- AND WARD, C. A. *Beiträge zur Chemie des Kautschuks. VI. Zur Theorie der Vulkanisation IV*. Koll. Zeit., 1913, 11, 274-80.
- AND YOUNG, J. *Comparison of Some Methods for the Estimation of Sulfur in Vulcanized Rubber with especial Reference to Electrolytic Oxidation*. J. Ind. Eng. Chem., 1912, 4, 413-17.
- *Apparat zur experimentellen Untersuchung der Heissvulkanisation*. Chem.-Ztg., 1912, 36, 1162-3.
- *Beiträge zur Chemie des Kautschuks. V. Zur Theorie der Vulkanisation III*. Koll. Zeit., 1912, 11, 28-34.
- *Beiträge zur Chemie des Kautschuks. VII. Zur Theorie der Vulkanisation V*. Koll. Zeit., 1913, 13, 265-71.
- SPILLER, J. *On the Oxidation of India-rubber*. Jour. Chem. Soc., 1865, 13, 44-6.
- SPRECHER, A. *Same und Keimung von Hevea brasiliensis*. Bull. du Jardin Bot. de Buitenzorg, 1915, No. XIX (2). 110 pp.
- SPRING, F. G. *Tapping and Tapping Systems*. Rep. Batavia, 1914, 155-160.
- *Tapping Systems*. Rubber Recueil, 1914, 303-13.
- STEFAN, M. J. *Anwendung der Schwingungen zusammengesetzter Stäbe zur Bestimmung der Schallgeschwindigkeit*. Sitzungsber. Wien, 1868, 57 (II Ab.), 697-708.
- *Anwendung des Chronoskops zur Bestimmung der Schallgeschwindigkeit im Kautschuk*. Sitzungsber. Wien, 1872, 65 (II Ab.), 419-23.
- STERN, E. *Ueber eine neue Methode zur Untersuchung der Heissvulkanisation des Kautschuks*. Zeit. f. Elektrochem., 9, 15, 660-1.

- STERN, E. *Ueber die Vulkanisation des Kautschuks*. Gummi-Ztg., 1913, 27, 623-6.
- . *Vulkanisation des Kautschuks und Strahlungsenergie*. Gummi-Ztg., 1913, 27, 1340.
- STÈVART, A. *Résultats d'Expériences sur l'Elasticité du Caoutchouc vulcanisé*. Bruxelles, Paris, 1888. 92 pp. (Gauthier-Villars); Bull. du Musée de l'Industrie de Belgique, 1870, 57, No. 5.
- STEVENS, H. P. *Der Einfluss der Stickstoffhaltigen und harzigen Bestandteile auf die Vulkanisierungsfähigkeit von Kautschuk*. Koll. Zeit., 1914, 14, 91-6.
- . *Estimation of Sulphur in Rubber*. Analyst, 1914, 39, 74-8.
- . *The Function of Litharge in the Vulcanization Process*. J. Soc. Chem. Ind., 1915, 34, 524-6.
- . *Determination of Sulphide and Sulphate Sulphur, and the Action of Solvents on Vulcanized Rubber*. Analyst, 1915, 40, 275-81.
- . *The Stability of Vulcanized Rubber and the Optimum Cure*. I.R.J., 1916, 52, 794.
- . *The Function of Litharge in the Vulcanization Process*. Influence of the Resins. J. Soc. Chem. Ind., 1916, 35, 874-7.
- . *The Stability of Vulcanized Rubber and the Optimum Cure*. J. Soc. Chem. Ind., 1916, 35, 872-4.
- . *Rubber Vulcanization Tests*. J. Soc. Chem. Ind., 1916, 35, 1141-2.
- . *The Natural Accelerator of Para Rubber*. J. Soc. Chem. Ind., 1917, 36, 365-70.
- . *The Vulcanization of Rubber by Agents other than Sulphur*. J. Soc. Chem. Ind., 1917, 35, 107-9.
- . *The Coefficient of Vulcanization and the State of Cure*. I.R.J., 1917, 53, 220-2.
- . *Comparative Methods for Determining the State of Cure of Rubber*. J. Soc. Chem. Ind., 1918, 37, 280-4 T.
- . *The Comparative Effect of Organic and Inorganic Accelerators in Vulcanizing Rubber*. J. Soc. Chem. Ind., 1918, 37, 156-8 T.
- . *Determination of Sulphur in Vulcanized Rubber*. Analyst, 1918, 43, 377-8.
- . *The Nature of Vulcanization*. J. Soc. Chem. Ind., 1919, 39, 192-6 T.
- TAKEUCHI, S. *Depolymerization of Raw Rubber*. J. Chem. Ind. Tokyo, 20, 1297-1309. (J. Soc. Chem. Ind., 1918, 37, 313 A; Chem. Abstrs., 1918, 1351.)
- TANGL, K. *Experimentaluntersuchungen über die Oberflächenspannung an der Trennungsfläche fest/flüssig*. Ann. der Phys., 1911, 34 (4), 311-42.
- TERRY, H. L. *Resinous Constituents of Caoutchouc*. J. Soc. Chem. Ind., 1889, 8, 173-5.

- THOMAS, P. *Contraction du caoutchouc par la chaleur*. Les Mondes, 1869, **19**, 579-9.
- . *Propriétés physiques du caoutchouc*. Les Mondes, 1869, **20**, 7-10.
- THOMSON, W. *India-rubber and its Decay*. J. Soc. Chem. Ind., 1885, **4**, 710-19.
- . *Notes on the Vulcanization and Decay of India-rubber*. Chem. News, 1890, **62**, 192-3.
- . *India-rubber (A Criticism)*. J. Soc. Chem. Ind., 1894, **13**, 473-6.
- AND LEWIS, F. *On the Action of Different Metals, Metallic Salts, Acids and Oxidizing Agents on India-rubber*. Mem. Manchester Lit. Phil. Soc., 1891, **4** (4), 266-81; Chem. News, 1891, **64**, 169-73.
- THURSTON, R. H. *Singular Stress-Strain Relations of India-rubber*. Science, 1897, **6**, 758-60; **7**, 522-3.
- TOCH, M. *The Influence of Pigments on Rubber*. J. Ind. Eng. Chem., 1917, **9**, 694-6.
- TOMLINSON, H. *On the Behaviour of Stretched Rubber when Heated*. Nature, 1886, **33**, 7-8.
- TORREY, J. *A Completely new Method for the Determination of Rubber*. I.R.J., 1905, **30**, 417-18.
- TROMP DE HAAS, W. R. *The Valuation of Para Rubber Trees by a Chemical Method*. Lects. on Rubber, 1908, 173-7.
- TSCHIRCH, A. AND SCHMITZ, W. *Ueber eine Methode zur Bestimmung der stickstoffhaltigen Nebenbestandteile des Rohkautschuks*. Gummi-Ztg., 1913, **26**, 2079-81.
- TUTTLE, J. B. AND ISAACS, A. *A Study of Recent Methods for the Determination of Total Sulfur in Rubber*. Bureau of Standards, Tech. Paper 45. 16 pp. (1915); J. Ind. Eng. Chem., 1915, **7**, 658-63.
- AND YURROW, L. *The Direct Determination of Rubber*. I.R.W., 1917, **57**, 17-18.
- TWISS, D. F. *Hydrochloric-ether Mixture as a Reagent for Rubber Analysis*. I.R.J., 1916, **50**, 199.
- . *C. O. Weber's Test for Sun-cracking*. I.R.J., 1916, **52**, 325.
- . *The Chemistry of Vulcanization*. J. Soc. Chem. Ind., 1917, **36**, 782-9.
- . *Vulcanization Catalysts*. J. Soc. Chem. Ind., 1917, **36**, 1072.
- AND BRAZIER, S. A. *The Acceleration of Vulcanization*. J. Soc. Chem. Ind., 1920, **39**, 125-32, 155-6T.
- UCHIDA, S. *Notes on some Fatty Oils (including Para Rubber Tree Oil)*. J. Soc. Chem. Ind., 1916, **35**, 1089-90.
- ULTÉE, A. J. *Caoutchouc*. Haarlem, 1913, 93 pp.
- . *Overzicht van de op Java genomen Bemestingsproeven bij Hevea (On Manuring Experiments made with Hevea in Java)*. Rubber Recueil, 1914, 339-44.

- ULTÉE, A. J. *Resultaten van viscositeitsbepalingen van rubber oplossingen*. Archief, 1918, 2, 331-44; 1919, 3, 24-33. (*Results of viscosity Determinations of Rubber Solutions.*)
- . *A Manuring Experiment on Poerwodjojo Estate*. I.R.J., 1918, 55, 683.
- . *Eenige gegevens over de mindere rubbersoorten*. Archief, 1919, 3, 412-16. (*Particulars about the Inferior Grades of Rubber*. Ibid., 417.)
- UNGER, B. *Ueber die Analyse des vulkanisierten Kautschuks insbesondere die Bestimmung des Schwefels in demselben*. Zeit. f. anal. Chem., 1885, 24, 167-74.
- UPTON, H. S. *Volumetric Determination of Free Sulfur in Soft Rubber Compounds*. J. Ind. Eng. Chem., 1918, 10, 518-20.
- UTZ. *Beitrag zur Bestimmung des Gesamtschwefels in Kautschuk*. Gummi-Ztg., 1918, 28, 631-2.
- VERNET, G. *Determination of the Caoutchouc of Latex of Hevea brasiliensis from Density Measurements*. (J. Soc. Chem. Ind., 1910, 29, 1464. Original: Le Caoutchouc, 1910, 7, 4549-58.)
- . *Sur les causes de la coagulation du latex d'Hevea brasiliensis*. Le Caoutchouc, 1920, 17, 10193-5.
- VILLARI, E. *Sulla elasticità del caoutchouc*. Cimento, 1869, 28 (2) 1, 332-52, 361-71. (*Ueber die Elasticität des Kautschuks*. Ann. der Phys., 1871, 143, 88-100, 290-305.)
- . *Sul calorico sviluppato nel caoutchouc per effetto della trazione*. Cimento, 2 (2), 301-6; Rend. Lomb., 2 (2), 760-72. (*Ueber die Wärme-Entwicklung beim Ausziehen des Kautschuks*. Ann. der Phys., 1872, 144, 274-80.)
- VRIENES, J. G. C. *Bodembeschrijving van de Rubberstreken ter Oostkust van Sumatra*. (*Description of the Soil of the Rubber Districts of the East Coast of Sumatra*.) Rubber Recueil, 1914, 171-82.
- DE VRIES, O. *Rubberonderzoek in het Centraal Rubberstation*. Meded. Centraal Rubberstation, No. 1, 1-20. (*Rubber Testing at the Central Rubber Testing Station at Builenzorg, Java*. I.R.J., 1916, 52, 717-19.)
- . *The Coefficient of Vulcanization as a Check on the State of Cure*. I.R.J., 1917, 101-3.
- . *Suiker als coagulatiemiddel bij crêpe bereiding*. Archief, 1917, 1, 5-13. (*Sugar as a Coagulant for Crêpe Rubber*. Ibid., 14-16.)
- . *Invloed van het mangelen bij de crêpe bereiding*. Archief, 1917, 1, 17-22. (*Influence of Rolling on Crêpe Rubber*. Ibid., 23-4.)
- . *Invloed van het rubbergehalte van de latex op de innerlijke eigenschappen van den rubber*. Archief, 1917, 1, 25-32. (*The Influence of the Rubber Content of Latex on the Inner Qualities of the Rubber*. Ibid., 33-4.)

- DE VRIES, O. *Invloed van de hoeveelheid azijnzuur op de innerlijke eigenschappen van den rubber.* Archief, 1917, 1, 35-9. (*Influence of the Amount of Acetic Acid on the Inner Qualities of the Rubber.* Ibid., 40-1.)
- *Invloed van den ouderdom der boomen op de eigenschappen van den rubber.* Archief, 1917, 1, 169-74. (*On the Influence of the Age of the Trees on the Quality of the Rubber.* Ibid., 175-7.)
- *Over het coaguleeren van den latex in gedeelten.* Archief, 1917, 1, 178-84. (*Partial Coagulation of Latex.* Ibid., 185-7.)
- *Over het verband tusschen soortelijk gewicht en rubbergehalte van den latex, ook met het oog op het gebruik van latex-aerometers (Metrolac enz.).* Archief, 1917, 1, 242-72. (*On the Relation between the Specific Gravity and Rubber-content of Latex, also with regard to the use of Hydrometers. (Metrolac, Latexometer, etc.)* Ibid., 273-9.)
- *Eenige opmerkingen over de eigenschappen van rubber afkomstig van boomen van één groep, en over den invloed van het tapsysteem.* Archief, 1917, 1, 280-6. (*Some Remarks on the Properties of Rubber from one group of Trees, and on the Influence of the Tapping System.* Ibid., 287-8.)
- *Iets over het vochtgehalte van Ondernemingsrubber op Java.* Archief, 1918, 2, 52-54. (*Moisture-content of Plantation Rubber in Java.* Ibid., 53-4.)
- *Invloed van enkele chemicaliën op de innerlijke eigenschappen van den rubber.* Archief, 1918, 2, 67-97. (*Influence of Certain Chemicals on the Inner Qualities of Rubber.* Ibid., 97-104.)
- *Over het bewaren (laten rijpen) van het coagulum.* Archief, 1918, 2, 213-34. (*On the Maturing of Coagulum.* Ibid., 235-40.)
- *Invloed van het openem van een tapsnede en van het op stomp kappen op latex en rubber.* Archief, 1918, 2, 241-51. (*The Influence of Opening a Tapping Cut and of Pollarding on Latex and Rubber.* Ibid., 252-5.)
- *De viscositeit van Plantage-rubber, haar samenhang met de eigenschappen na vulcanisatie, en haar beteekenis voor het rubberonderzoek.* Archief, 1918, 2, 456-79. (*The Viscosity of Plantation Rubber, its Relation to the Properties after Vulcanization, and its Significance in Rubber Testing.* Ibid., 481-7.)
- *Invloed van zwaar tappen op latex en rubber.* Archief, 1918, 2, 437-52. (*Influence of Heavy Tapping on Latex and Rubber.* Ibid., 453-5.)
- *Veranderingen in ge vulcaniseerd rubber bij verhoogde temperatuur.* Archief, 1918, 2, 792-801. (*Changes in Vulcanized Rubber at Elevated Temperatures.* Ibid., 802-6.)



- DE VRIES, O. *Some Remarks on the Ageing of Vulcanized Rubber.* I.R.J., 1919, 57, 77-81.
- . *Verband tusschen het soortelijk gewicht van latex en serum en het rubbergehalte van de latex.* Archief, 1919, 3, 183-201. (*The Relation between the Specific Gravity of Latex and Serum and the Rubber-content of Latex.* Ibid., 202-6.)
- . *Over de bruikbaarheid van instrumenten als Metrolac en Latexometer voor het bepalen van het rubbergehalte van de latex.* Archief, 1919, 3, 207-17. (*On the Use of Hydrometers—Metrolac, Latexometer—to Determine the Rubber-content of Latex.* Ibid., 218-21.)
- . *Latex en rubber van onder- en bovensnede.* Archief, 1919, 3, 124-7. (*Latex and Rubber from Upper and Lower Cut.* Ibid., 128-9.)
- . *Invloed van verandering van tapvlak op latex en rubber.* Archief, 1919, 3, 130-6. (*Influence of a Change of Tapping Surface on Latex and Rubber.* Ibid., 137-8.)
- . *The Use of Hydrometers to Determine the Rubber-content of Latex.* I.R.J., 1919, 81-2.
- . *Invloed van het Uitrekken met water op de Eigenschappen van den rubber.* Archief, 1919, 3, 339-68. (*Effect of Soaking the Rolled or Unrolled Coagulum in Water on the Properties of the Rubber.* Ibid., 369-73.)
- AND HELLEDOORN, H. J. *On the Permanent set of Rubber.* J. Soc. Chem. Ind., 1917, 38, 1258-62.
- . *Gewichtsverschillen bij sheet en crêpe bereiding.* Archief, 1918, 2, 361-86. *Proeven over de bereiding van smoked sheet en crêpe op eene onderneming.* Archief, 1918, 2, 387-92. (*Differences in Weight in the Preparation of Sheet and Crêpe Rubber.* Ibid., 393-400.)
- . *Invloed van rustiness op de innerlijke eigenschappen van sheet rubber.* Archief, 1918, 2, 527-35. (*Influence of Rustiness on the Inner Qualities of Sheet Rubber.* Ibid., 536-8.)
- . *Invloed van verwarming op de innerlijke eigenschappen van den rubber.* Archief, 1918, 2, 539-56. (*Influence of Heat on the Inner Qualities of Rubber.* Ibid., 557-60.)
- . *De Trekvastheid bij rubber-zwavel mengsels.* Archief, 1918, 2, 769-84. (*The Tensile Strength of Rubber-Sulphur Mixtures.* Ibid., 785-91.)
- . *Verloofig overzicht van de eigenschappen van rubber van diverse kwaliteiten.* Archief, 1917, 1, 213-29. (*Preliminary Review of the Properties of Rubber of Different Grades.* Ibid., 230-3.)
- AND SPOON, W. *Veranderingen in ge vulcaniseerden rubber kort na de vulcanisatie.* Archief, 1918, 2, 807-13. (*On the Changes in Vulcanized Rubber during the First Days after Vulcanization.* Ibid., 814-16.)

- DE VRIES, O., AND SPOON, W. *Variabiliteit van Plantage-Rubber*. *Archief*, 1919, 3, 246-65. (*Variability in Plantation Rubber*. *Ibid.*, 266-76.)
- WAGNER, A. *Ein Beitrag zur Kenntnis der kolloidalen Natur des Kautschuks*. *Chem.-Ztg.*, 1912, 36, 833.
- WARBURG, E. *Ueber die Dämpfung der Töne fester Körper durch innere Widerstände*. *Ann. der Phys.*, 1870, 139, 89-104.
- WEBER, C. O. *Zur Analyse der Kautschukwaren*. *Chem.-Ztg.*, 1894, 18, 1003-5, 1040-1, 1064-9.
- . *Ueber die Vulkanisation des Kautschuks*. *Chem.-Ztg.*, 1894, 18, 837-8, 1695-6.
- . *On the Analysis of India-rubber Articles*. *J. Soc. Chem. Ind.*, 1894, 13, 476-85.
- . *On the Vulcanization of India-rubber*. *J. Soc. Chem. Ind.*, 1894, 13, 11-17; 1895, 14, 436-43.
- . *Zur Analyse vulkanisierter Kautschukwaren*. *Zeit. angew. Chem.*, 1898, 313-15.
- . *The Nature of India-rubber*. *J. Soc. Chem. Ind.*, 1900, 19, 215-21.
- . *Ueber die Natur des Kautschuks*. *Ber.*, 1900, 33, 779-96; 1902, 35, 1947-57.
- . *Reise nach einer Kautschukplantage in Columbien*. *Dresden*, 1902.
- . *The Chemistry of India-rubber*. London, 1902. (Griffin.)
- . *Grundzüge einer Theorie der Kautschuk-vulkanisation*. *Dresden*, 1902. (Steinkopff u. Springer.)
- . *Theory of Vulcanization of India-rubber*. (*J. Soc. Chem. Ind.*, 1902, 21, 712-13. Original: *Gummi-Ztg.*, 1902, 16, 561-4.)
- . *Zur Analyse des Kautschuks und der Kautschukwaren*. *Ber.*, 1903, 36, 3103-8.
- . *Zur Chemie des Kautschuks*. *Ber.*, 1903, 36, 3108-15.
- . *Ueber die Methode zur Wertbestimmung des Kautschuks*. *Gummi-Ztg.*, 1903, 18, 461.
- . *Eine neue Methode der Kautschukanalyse*. *Gummi-Ztg.*, 1903, 18, 339-341, 521-3.
- . *Ueber das Verhalten des Kautschuks gegen Metalle*. *Gummi-Ztg.*, 1903, 18, 255-6.
- . *Action of Light on India-rubber*. *I.R.J.*, 1903, 25, 639.
- . *Coagulation of India-rubber Latex*. *I.R.J.*, 1903, 26, 19.
- . *Influence of Liitharge on Hot Vulcanization*. (*J. Soc. Chem.*, 1903, 22, 103. Original: *Gummi-Ztg.*, 1903, 17, 296.)
- . *The Vulcanization Process*. (*J. Soc. Chem. Ind.*, 1903, 22, 809. *Gummi-Ztg.*, 1903, 17, 812.)
- . *Use of Chloral Hydrate in Rubber Analysis*. *I.R.J.*, 1903, 25, 375.
- . *Properties of Sulphur or Vulcanizing India-rubber*. *I.R.J.*, 1904, 27, 21, 30.

- WEBER, C. O. *Ueber die Milch von Castilloa elastica und deren Koagulation.* Gummi-Ztg., 1905, **19**, 101-4.
- . *Zur Frage der Kautschukkoagulation und Kautschuklöslichkeit.* Gummi-Ztg., 1905, **19**, 354-6.
- WEBER, L. E. *The Action of the Resins in the Vulcanizing of Rubber.* 8th Internat. Cong. Appd. Chem., 1912, **9**, 95-9.
- . *Increase of the Resins in the Vulcanization.* I.R.W., 1916, **55**, 6.
- WELEKER, W. H., BEAL, G. D. AND GEIGER, G. A. *Diffusion through Rubber Membranes.* Biochem. Bull., 1912, **2**, 55-86.
- WERTHEIM, G. *Mémoire sur l'équilibre des corps solides homogènes.* Ann. de chim. phys., 1848, **23** (3), 52-95.
- WESSELS, H. *Ueber Thermolyse. Das Ludwig-Soretische Phänomen in fester Körpern.* Zeit. phys. Chem., 1914, **87**, 215-52.
- WESSON, L. G. *Preliminary Note on a New Method for the Direct Determination of Rubber.* J. Ind. Eng. Chem., 1913, **5**, 398.
- . *The Combustion Method for the Direct Estimation of Caoutchouc.* J. Ind. Eng. Chem., 1914, **6**, 459-62.
- AND KNORR, E. S. *Wet Combustion in the Nitrosite Combustion Method for the Direct Estimation of Caoutchouc.* J. Ind. Eng. Chem., 1917, **9**, 139-40.
- WHEATLEY, R. AND PORRITT, B. D. *A New Machine for the Preparation of Vulcanized Rubber for Analysis.* J. Soc. Chem. Ind., 1915, **34**, 587-8.
- WHITBY, G. S. *On some Preliminary Observations regarding the Causes of Natural Change in the Latex of Hevea brasiliensis; and on the Depolymerization of Caoutchouc and its Conversion.* 8th Internat. Cong. Appd. Chem., 1912, **25**, 597-621. (In German: Koll. Zeit., 1913, **12**, 147-57, 190-3.)
- . *A few Points regarding Smoked Rubber.* Rep. Batavia, 1914, 164-71.
- . *The Prime Technical Plantation Problems of the Next Decade.* Internat. Rubber Cong., Batavia, 1914. 29 pp.
- . *Some Notes on Standardization.* I.R.J., 1914, **48**, 805.
- . *A Comparison of the Brazilian and Plantation Methods of Preparing Para Rubber.* J. Soc. Chem. Ind., 1916, **35**, 493-500.
- . *Moisture in Raw Rubber.* J. Soc. Chem. Ind., 1918, **37**, 278-80 T.
- . *Theory of Latex Coagulation.* Agric. Bull. F.M.S., 1918, **6**, 374-84.
- . *Note on Bacterial Changes in Latex.* Agric. Bull. F.M.S., 1918, **6**, 513-16.
- . *Variation in Hevea brasiliensis.* Ann. Bot., 1919, **31**, 313-21.
- WILLIAMS, W. A. *The Advantages and Defects of Plantation Rubber.* Rubber Industry, 1914, 284-97.

- WORMELEY, P. L. *Some Apparatus for Tension Tests of Rubber*. Proc. 6th Cong., Internat. Assocn. for testing materials, New York, 1912, XXII<sub>3</sub>. 12 pp.
- . *Notes on Tension Tests for Rubber*. Rubber Industry, 1914, 416-21.
- . *The Influence of Temperature on the Tensile Properties of Rubber Compounds*. Rubber Industry, 1914, 246-58.
- WOUDSTRA, H. W. *Ueber die Viscosität und die Koagulation von Kautschuklösungen*. Koll. Zeit., 1909, 5, 31-2.
- WRIGHT, H. C. *Rubber Soils in Fiji*. Dept. Agric. Fiji, Pamphlet No. 26, 1917. 2 pp.
- WRIGHT, H. *Hevea brasiliensis, or the Para Rubber Tree; Its Botany, Cultivation, Chemistry and Diseases*. 4th Edit., London and Colombo, 1912.
- . *The Science of Para Rubber Cultivation*. Colombo, 1907. 100 pp.
- WROBLESKI, S. v. *Ueber die Natur der Absorption der Gase*. Ann. der Phys., 1879, 8, 29-52.
- YATES, H. S. *The Growth of Hevea brasiliensis in the Philippine Islands*. Philippine Jour. Sc., 1919, 14, 501-23.
- ZILCHERT, P. *Zur Kenntnis der Kautschukharze*. Gummi-Ztg., 1911, 25, 716-17.
- ZOTT, A. *Ueber die relative Permeabilität verschiedener Diaphragmen und deren Verwendbarkeit als dialytische Scheidewände*. Ann. der Phys., 1886, 27, 229-89.

1506

678

FO

## INDEX OF SUBJECTS

- ABBREVIATIONS, xv
- Absorption of light by rubber, 476
- Accelerators, artificial, 196-200; influence of, on progressive combination of sulphur, 315; influence of, on vulcanization coefficient, 359; inorganic, 392, 393 *et seq.*; in matured rubber, 189; natural, 195; natural and artificial, comparison of, 196; in latex, 195
- Acetaldehyde in latex, 70
- Acetic acid, 144; influence of, excess on vulcanization, 145
- Acetone, extraction by, 81
- Acetone extract, diminution of, on vulcanization, 77. *See also* Resin.
- Acid, admixture of, with latex, 154
- Adsorption of resin, 81
- Adsorption theory of vulcanization, 306
- After-effect, influence of, an exceptional strain on, 442; law of, 434-5, 437, 443; in successive cycles, 436
- After-effects, superposed, 426, 433
- After-retraction, 429, 446. *See also* Set; and after-strain, comparison of, 431, 440
- After-strain, 430, 433, 438 *et seq.*, 446; influence of quality of rubber on, 446; Poisson's ratio for, 495; and after-retraction, comparison of, 431, 440
- Age of trees, influence of, on quality, 210
- Ageing, 367, 368-71. *See also* Vulcanization at low temperatures; accelerated, 371-80; change of stress-strain curve during, 375-9; influence of percentage of sulphur on, 381
- Alkalis, 197
- Alum, 144, 148
- Ammonia, 37, 129, 196
- Amyrin, 78
- Anaerobic natural coagulation, 52; influence of sugars on, 53
- Analyses of latex, early, 57
- Anisotropy of stretched rubber, 473
- Anti-coagulants, 127 *et seq.*; influence of, on vulcanizing properties, 129
- Area under rubber, vii
- Ash, amount of, in raw rubber, 59
- Attalea excelsis*, 201
- Autoclave, vulcanization in, 294
- Autoxidation of caoutchouc, 97
- Bacterial activity in latex, 52
- Bark. *See* Cortex.
- Bark crêpe, 167
- Bark, rubber *in situ* in, 9
- Bark rubber, tacky, 103
- Bark shavings, 124
- Barytes, 499
- Block rubber, 204
- Boric acid, 188
- Bornesitol, 66
- Branching, induced, 14
- Brazil, *Hevea* varieties in, viii
- Brazilian method on plantations, 203
- Brazilian rubber, comparison of, with plantation, 201-3
- Breaking figures, fortuity in, 275, 319, 327, 343-5
- Breaking point as index to state of cure, 379
- Brownian movement, 32
- Bubbles in sheet, 174-6
- Bulking, 143, 214
- Byrne process, 173
- Calcium malate, 72
- Calcium salts and natural coagulation, 51
- Calender, 287
- Calendered sheet, grain in, 484
- Caoutchouc, direct determination of, 59; oxidation of, 79, 95
- Carbon black, 499, 500
- Casein, influence on vulcanization, 122, 123
- Catalase in Fine Para, 55
- Catalysts, vulcanization, 189
- Chemical analysis and evaluation of raw rubber, 281, 282

- Chemical composition of latex, 57  
*et seq.*; of rubber, 58 *et seq.*  
 China clay, 499  
 Chlorogenic acid, 71  
 Citric acid, 147  
 Climate, vii  
 Clot, microscopic character of, and  
 vulcanizing properties, 40  
 Coagulating enzyme, 46  
 Coagulation, anaerobic, 148-50;  
 cause of, 40-8; electrical, 32;  
 external features of, 39; incom-  
 plete, 146; influence of salt con-  
 centration on, 35; natural,  
 cause of, 50; partial, 132; trial,  
 139. *See also* Anaerobic natural  
 coagulation.  
 Coagulation by acetic acid, 144;  
 by hydrochloric acid, 47  
 Coagulation of latex and of milk,  
 analogies between, 47; by nitric  
 acid, 48; of preserved latex, 34;  
 and protein, 43  
 Coco-nut sap, 147  
 Coefficient of vulcanization, 303;  
 determination of, 308  
 Collection of latex, 126-7  
 Colophony, influence on vulcaniza-  
 tion, 85  
 Comparison of samples in rubber-  
 sulphur mixes, 385  
 Compounded rubber. *See* Mineral-  
 ized rubber.  
 Compounding ingredients, 398;  
 passive, 391  
 Compressibility, 501  
 Compression, stress-strain relations  
 on, 249-52  
 Copper, deterioration produced by,  
 104; oxidation of caoutchouc  
 under influence of, 97  
 Correct cure, 354. *See also* Op-  
 timum cure.  
 Cortex, 8; anatomy of, and rubber  
 yield, 7-9  
 Crêpe, 147, 151 *et seq.*, 184; bark,  
 167; compound, 167; earth, 167,  
 gristly, 164; influence of thick-  
 ness on vulcanization of, 158;  
 lower grade, 165; moisture in,  
 163; paleness in, 151; scrap,  
 166; smoked, 183; spotted, 160;  
 thick, 159  
 Crêpe and sheet, comparison of,  
 184, 205, 208  
 Crêping, 155; influence on vul-  
 canizing properties, 157; dry  
 rubber, 289  
 Cresol, 181  
 Cross section of test pieces, 270-5  
 Curdling temperature, 46  
 Cuts, lower and upper, 211; new,  
 209, 212  
 Cutting test pieces, 298  
 Cycles, after-effect in a succession  
 of, 436; influence of periods of  
 rest on after-effect on, 437;  
 length of, 413; repetition of,  
 411; successive, law of, 413; and  
 evaluation of rubber, 419-22  
 Cycles of extension and retraction.  
*See* Cycles.  
 Cyclic fatigue, 420; remainder, 420  
 Cyclic tests. *See* Cycles.  
 Dambonitol, 65, 66  
 Decay of tension, 445  
 Depolymerization. *See* Disaggre-  
 gation.  
 Desiccation of latex, 46  
 De-vulcanization, 303  
 Dialysed latex, coagulation of, 35  
 Dichromatism, 476  
 Dielectric constant, 478; change  
 of, on stretching, 483  
 Dies, 298  
 Dilution of latex, 141-4; to stan-  
 dard, 141; and vulcanizing  
 properties, 141  
 Disaggregation, 102, 105-7, 112 *et*  
*seq.*; and oxidation, 102, 105;  
 and tackiness, 102, 105  
 Diseases, tree, 4  
 Double refraction in rubber, 474-6  
 Drying, hot-air, 164; crêpe, 162-5  
 Earth crêpe, 167  
 Earth rubber, 124; tacky, 103  
 Elastic after-effect. *See* After-  
 effect.  
 Elastic limit, 219  
 Elastic modulus. *See* Modulus of  
 elasticity.  
 Electric field, mechanical deforma-  
 tion of rubber in a, 479-83, 484  
 Electrical coagulation, 32  
 Electrification on deformation, 477  
 Electrostriction, 479-83  
 Elongation, measurement of, 267  
 Enzyme, coagulating, 50  
 Enzymes, oxidizing in latex, 54  
 Evaluation mix, 380 *et seq.*  
 Evaluation of raw rubber, methods  
 of, 281  
 Experiments, field, 28-30  
 Fast- and slow-curing rubber, com-  
 parison of, 333-6  
 Fertilization, cross, 11  
 Field experimentation, 28-30

- Fillers, 391  
 Fine Hard Para, 201, 203  
 Flattening rubber sphere, 244  
 Food reserves and tapping, 21  
 Formaldehyde, 128, 130-1, 188, 204  
 Formaldehyde as latex preservative, 37  
 Formic acid, 147  
 Freezing latex, 148  
  
 Girth and yield, 13  
 Globules, behaviour of, in coagulation, 38-9; occurrence of, in rubber, 39  
 Glucoside, cyanogenetic, in seed, 4  
 Glyco-protein, 109, 115, 117  
 Grades, proportions of, 124-5  
 Grain, 265  
 Grips, 259, 262  
 Growth of tree, 11-12  
 Guanidines, 190  
  
 Hexamethylenetetramine, 199  
 Hooke's law, 219, 224  
 Hydrochloric acid, 47, 147  
 Hydrocyanic acid, 51, 70  
 Hydrofluoric acid, 147  
 Hydrometers. *See* Laticometers.  
 Hysteresis, 410 *et seq.*, 500. *See also*  
   Cycles; compression, 250, 251-2;  
   methods of studying, 411, 417;  
   loops, 412 *et seq.*, 422  
  
 Impact of cylinders, 245-7  
 Impact tests, 248  
 Inorganic constituents, fixation of sulphur by, 389; influence of, on stress-strain curve, 398; influence of, on vulcanization coefficient, 360  
 Inorganic constituents, progressive curing of mixes containing, 388  
 Inorganic constituents of latex, 62  
 Inositol and derivatives, physiological significance of, 68  
 Inositol derivatives in latex, 65 *et seq.*  
 Insoluble constituent of rubber. *See* Protein.  
 Instability of rubber, 367  
  
 Jelutong resin, 77; influence of, on vulcanization, 85  
 Joule effect, 453, 460; cause of, 459 *et seq.*, 470, 472  
  
 Lampblack, 499, 500  
 Latex, Brownian movement in, 32; chemical composition of, 57 *et seq.*; analogy of, with milk, 45; collection of, 126-7; determination of rubber-content of, 135-41; dilution of, 141; fractional extraction of, with ether, 81; natural changes in, 49; oecology of, 26; oxidases in, 54; physiological function of, 23-8; place of formation of, 24, 27; point of origin of, 16; pre-existence of caoutchouc in, 41-3; preserved, 37; preserved, coagulation of, 34; protective function of, 27; reaction of, 49; rubber-content of, 5; specific gravity of, 65, 137; viscosity of, 33  
 Latex from base of leaves, composition of, 61; from early tapplings, 31; emulsoid or suspensoid, 33; as foodstuff, 24-6; globules, 31; globules, electrical charge on, 32; specific gravity of, 43; tanks, 142; vessels, 8-9, 18, 24, 28  
 Latexometer. *See* Laticometers.  
 Laticometers, 135-8  
 Leucine, 190  
 Life-curve of rubber, 368  
 Lime, 142, 361, 390, 392  
 Litharge, 389, 392, 393, 399  
 Litharge, 389, 392, 393, 399; comparison of, with magnesia, 394, 396  
 Load-stretch curve. *See* Stress-strain curve.  
 Loss on washing, 59  
 Low grades, washing, 165  
 Lump, 125-6, 131-5; paleness in, 132; uniformity of, 134; vulcanizing properties of, 132  
 Lupeol, 78  
  
 Machines. *See* Mills.  
 Machining. *See* Crêping.  
 Magnesia, 361, 362, 389, 390, 392, 393, 395, 399; comparison of, with litharge, 394, 396; degree of fineness of, 395  
 Manuring, 14  
 Maturation, 186 *et seq.*; factors influencing, 194; loss of nitrogen in, 191; period required for, 187  
 Maturation and acetone extract, 94  
 Matured rubber, uniformity of, 194; vulcanizing properties of, 193  
 Mercuric chloride, 188  
 Metrolac. *See* Laticometers.  
 Micrometer, 295  
 Mills, 156, 165  
 Mineralization, influence of, on hysteresis loops, 422

- Mineralized rubber, stress-strain curves for, 223
- Mixing, 290
- Mixing operations, uniformity of, 291
- Modulus of elasticity, 224-45; definition of, 224-5, 226; determination of, by oscillation of suspended weight, 244; determination of, by stationary waves, 242; determination of, by velocity of sound, 242, 461; dynamical determination of, 229-31; hysteresis in, 244; influence of length of cycle on, 238; influence of periods of repose on, 238-40, 244; influence of rate of extension and retraction on, 241; influence of temperature on, 460-70; statical determination of, 235-7
- Modulus of elasticity of calendered sheet, 484; at different extensions, 226, 232-4; at small extensions, 227, 234; throughout cycles, 232-4, 237, 242
- Moisture in raw rubber, 163, 183
- Molecular weight of caoutchouc from latex, 42
- Moulds, 295, 297
- Muscular contraction, analogy of, with Joule Effect, 473
- Nephelometer, 138
- Nitric acid, 48
- Nitrogen in raw rubber, 59; determination of, by Kjeldahl's method, 114; diffusible, in latex, 62, 64; in acetone extract, 92-4
- Nitrogen and maturation, 191
- Nitrogen-content and rate of vulcanization, 123
- Nitrosodimethylaniline, 190, 198, 199, 394
- Oil of rubber seed, 3
- Oil-bath vulcanizer, 296
- Optical relations of rubber, 474
- Optimum cure, 342, 347-56, 358
- Optimum curves, 317, 322, 347, 348, 354, 356, 381
- Oxalic acid, 147
- Oxidase activity and acid, 57; substances accelerating, 57; and vulcanizing properties, 56
- Oxidases in latex, 54; in rubber, 55, 56
- Oxidation of caoutchouc, 79, 95, 102; of gutta-percha, 95; and tackiness, 101
- Oxidizability of caoutchouc, 98
- Packing, 216
- Pans, sheet, 168
- Para, Fine Hard, 201, 203
- Pentachlorethane, 113, 114
- Peptone, influence of, on vulcanization, 122
- Perfect cure, 381. *See also* Optimum cure.
- Permanent set. *See* Set.
- Phenol, 181, 188, 204
- Pineapple juice, 147
- Piperidine, 196, 394
- Piperidine piperidyl dithiocarbamate, 199, 359
- Planting distances, 12
- Poisson's ratio, definition of, 486, 490; measurements of, 487, 488, 491, 493, 494, 495, 496; methods of determining, 487, 494-5; mode of calculating, 490-4
- Poisson's ratio for after-strain, 495; in different directions, 496. *See also* Volume increase on stretching.
- Porosity, 297
- Pre-existence of caoutchouc in latex, 41-3
- Preserved latex, coagulating enzyme in, 48
- Press, vulcanization, 294
- Previous stretching, influence of, on tensile tests, 278
- Pre-vulcanization, 316
- Probable error in breaking figures, 319, 327, 343
- Production, statistics of, v-vi
- Protein, 108 *et seq.*; average amount in raw rubber, 59; chemical character of, 117; distribution of, through fine Para, 110; influence of, on oxidation of caoutchouc, 99; influence of, on vulcanization, 120 *et seq.*; methods of separating, 112
- Protein and coagulation, 43
- Protein sheath round globules, 43
- Pulley supports, rotation of, 275-7
- Putrescine, 190
- Pyroligneous acid, 181
- Pyrrolidine, 190
- Quebrachitol, 65, 67; amount of, in latex, 63; influence of, on oxidation of caoutchouc, 99; influence of, on vulcanization, 72
- Rainfall and yield, 16
- Rate of cure, 342, 347; variation in, 207
- Rate of deformation, 415



- Rate of extension, influence of, on tensile tests, 277; influence of, on after-effect, 440  
 Rate of tracing cycles, 415  
 Rebound, 337  
 Recovery. *See* After-retraction.  
 Red oxide, 499  
 Residual acidity, 60  
 Resin, rubber, 76 *et seq.*; adsorption of, 81; average amount of, in raw rubber, 59; combination of sulphur with, 77; influence of, on rate of combination of sulphur, 91; influence of, on oxidation of caoutchouc, 98; influence of, on stress-strain curve, 86, 90, 91; influence of, on viscosity, 95; influence of, on vulcanization, 82 *et seq.*; influence of, on vulcanization with litharge, 91-2; iodine number of, 77; Jelutong, 77; mode of occurrence in latex and rubber, 80; nitrogen in, 92-4; optical inactivity of, 76; physiological significance of, 79; saponifiability of, 76; and oxidation of caoutchouc, 79; and stability of vulcanizate, 88  
 Resin-content, change of, during ageing, 373  
 Rest before tensile testing, 299  
 Reversion of stress-strain curve, 331, 397  
 Ribbing sheet, 172  
 Rigidity, 253  
 Rolling. *See* Crêpe.  
 Rolling sheet, 172  
 Rustiness, 176-8  
  
 Saccharic acid, 72  
 Scrap, 124  
 Scrap crêpe, 166  
 Schwartz machine, 418  
 Seed, collection of selected, 10  
 Seed glucoside, 4  
 Seed oil, 3  
 Seed selection, 4 *et seq.*  
 Selenium, 286  
 Serum, composition, 65  
 Set, 219, 337-9, 448-52; influence of temperature on, 280; relation of, to slope, 352, 450  
 Set. *See* After-effect.  
 Shavings. *See* Bark shavings.  
 Sheet, 147, 168 *et seq.*, 184; bubbles in, 174-6; maturation of, 191; moisture in, 183; resinous. *See* Rustiness; rusty, 176-8; tanks, 168-72; tensile tests on, 283-4  
 Sheet, smoked, colour of, 173; smoked. *See* Smoking sheet; thickness of, 170  
 Sheet and crêpe, comparison of, 184  
 Shrinkage of coagulum, 171  
 Skimmings, 154, 171  
 Slab, 187. *See also* Matured rubber.  
 Slope, 349; method of expressing, 351; relation to set, 353, 450; significance of, 352; variation in, 207  
 Slope of lower grades, 167; and maximal tensile strength, 354  
 Slow- and fast-curing rubber, comparison of, 333-6  
 Smoke, water-soluble constituents of, 181; phenolic constituents of, 181  
 Smoking sheet, 172, 178  
 Sodium acetate, 154; bisulphite, 151-4; bisulphite, amount of used, 151; carbonate, 128, 129; hydroxide, 197; sulphite, 128, 129  
 Soils, rubber, 14  
 Solutions, condition of protein in, 111, 120  
 Solvents, behaviour of, towards rubber, 110  
 Sound, velocity of, in rubber, 245, 247  
 Specific gravity of latex, 137; of serum, 65  
 Spiller's resin, 95  
 Spots in crêpe, 160  
 Stability of vulcanizates. *See* Ageing.  
 Staining protein in rubber, 109  
 Starch, depletion of, 22; influence of, on vulcanization, 122  
 State of cure, 340  
 Sterols in rubber, 79  
 Stress-strain curve, 221 *et seq.*; change of, with progress of vulcanization, 317, 320; as index to state of cure, 342-8, 379; influence of compounding on, 223, 398; mathematical expression for, 353 *et seq.*, 356; and shape of test piece, 268, 270; for mineralized rubbers, 223; typical, 222; standard. *See* Optimum curves.  
 Stress-strain relations, uniqueness of, 219  
 Stretching, repeated, 339  
 Structure, intimate, of rubber, 255-8  
 Sugar, 148; and anaerobic natural coagulation, 53; in latex, 61  
 Sulphate sulphur, 390  
 Sulphide sulphur, 390

- Sulphur, free, 303; free, determination of, 308; combined, 302, 303; combined, removal of, 303-4; combination of, with inorganic constituents, 389; determination of, 308-13; percentage of, influence of, on maximal tensile properties, 381, 383; percentage of, influence of, on rate of vulcanization, 324; influence of, on maximal tensile strength, 327; influence on stability of vulcanizate, 381; progressive combination of, with caoutchouc, 313, 319
- Sulphur coefficients, 361
- Sulphuric acid, 147
- Sulphurous acid, 154
- Sunlight, 372
- Supports for test piece, 275-7
- Swelling, influence of, on tensile properties of raw rubber, 284
- Tackiness, 100 *et seq.*; and disaggregation, 105
- Talc, 392
- Tanks, latex, 142; sheet, 168-72
- Tannin and tackiness, 102
- Tannic acid, coagulation by, 45
- Tapping, 15-22
- Tapping. *See also* Variation, physiological factors in. *See also* Yield.
- Tapping and food reserves, 21
- Tapping system, influence of, on vulcanization, 210
- Tartaric acid, 147
- Technical mixes, variation in, 399
- Temperature, influence of, on after-effect, 431; influence of, on cycles, 417; influence of, on rate of vulcanization, 321-4; influence of, on tensile tests, 279
- Temperature coefficient of vulcanization, 374
- Tensile product, 348, 349
- Tensile properties, sharpness of maximal, 325-36; progressive change of, on vulcanization, 315-21
- Tensile strength, variation in, 205. *See also* Breaking figures.
- Tensile testing machines, 268
- Tensile tests, test period preceding, 299; technique, 259 *et seq.*; on raw rubber, 283
- Test pieces, cross section of, 263, 270-5; dumb-bell, 260, 262 *et seq.*, 288, 298; looped, 259; most advantageous shape of, 262-70; ring, 259, 262 *et seq.*, 288, 299; straight, 260, 262 *et seq.*
- Testing machines, 268
- Tetrahydropyrrole, 190
- Tetramethylenediamine, 190
- Thermal effects of mechanical deformation, 453-6; expansion of rubber, 470
- Thermo-elastic behaviour, 453-9; points of inversion in, 456, 458
- Thinning-out, 12-13
- Thymol, 51
- Toluene, 51
- Torsion, 252-5, 464
- Torsional after-effect, 424
- Tree scrap. *See* Scrap.
- Trees, species of rubber, vii-viii
- Trichloroacetic acid, 113, 116
- Type. *See* Slope.
- Tyrosine, 191
- Ultra-violet rays on rubber, 102
- Urucuri nut, 201
- Vacuum drying, 163, 164
- Valuation of raw rubber, 282
- Variation, 201 *et seq.*; and bulking, 214; extent of, 204-8; factors producing, 208; and field experimentation, 29; in lump, 134; in matured rubber, 194; in rubber yield, 5-11; in technical mixes, 399; and packing, 216; physiological factors in, 208-13
- Velocity of sound in rubber, 461-2
- Vinegar, rice, 147
- Viscosity, factors in rubber preparation influencing, 408-9; of fractional solutions, 403; index, 405; influence of light on, 404; influence of resin on, 95; influence of shaking on, 403; influence of working on, 404; of latex, 33; measurement of, 403; methods of expressing, 404; number, 404; relation of, to tensile properties of raw rubber, 285; variation in, 207; and vulcanizing properties, 402, 405
- Volume increase on stretching, 488-90, 497-500; demonstration of, 500; influence of compounding ingredients on, 497-501; influence of prior history on, 489
- Vulcanization at low temperatures, 83, 371-5; by organic compounds, 307; by rising temperatures, 315

- Vulcanization, changes produced by, 286; coefficient of, 303; cold, 287; discovery of, 286; methods of, 293; nature of, 305; progressive, of mixes containing inorganic constituents, 388; progressive change of tensile properties on, 315; temperature coefficient of, 305
- Vulcanization coefficient at optimum cure, 358; determination of, 308-13; influence of organic accelerators on, 359; and state of cure, 358-66
- Vulcanization operations, outline of, 286; testing, outline of, 73 *et seq.*
- Vulcanizing quality, 302
- Washing dry rubber, 289; lower grades, 165
- Water, hot, on sheet, 177
- Whiting, 499
- Wintering, 22
- Working. *See* Crêping.
- Working, influence of, on viscosity, 404
- Working dry rubber, 292. *See also* Mixing.
- Wound response, 16
- Yield and height of cut, 18; and length of cut, 20; and number of cuts, 19; and obliquity of cut, 21; and rainfall, 16; and tapping interval, 20
- Young's modulus. *See* Modulus of elasticity.
- Zinc oxide, 361, 388, 390, 391, 399, 499

# INDEX OF AUTHORS' NAMES

- Adriani, 95  
 Alexander, 77, 79  
 Alexrod, 292, 403  
 Amagat, 490  
 Arens, 13, 177  
 Arisz, 16  
 Auerbach, 92  
  
 Barritt, 35  
 Barrowcliff, 14, 29, 46, 50-1, 150  
 Bary, 72  
 Bateson, 20, 21, 23, 27  
 Beadle, 31, 32, 37, 38-9, 40, 42, 45, 48, 61, 80, 84, 111, 119, 120, 152, 248-9, 275, 277, 391-2, 413, 419-20, 448  
 Bellati, 494  
 Bernard, 24  
 Bernstein, 102, 106  
 Bertels, 130  
 Biffen, 44, 144  
 Bishop, 29  
 Bjerken, 255, 457, 474-5, 493  
 Bobiloff, 8, 10, 24, 27, 28, 31  
 Bobiloff, Sr., 28, 49  
 Boggs, 286  
 Boileau, 249-50, 410  
 Boltzmann, 245-6  
 Borrowman, 33, 141  
 Bouasse, 228-41, 242-4, 262, 277, 411-17, 435-45, 457, 461, 465, 467-9, 489, 491  
 Bouchet, 481, 482, 495-6  
 Bourn, 323  
 Braendle, 484  
 Breuil, 251, 272, 337  
 Bryce, 7, 8, 18  
 Bunschoten, 107, 286  
  
 Campbell, 7, 8, 15, 18, 20, 21, 22, 39, 50, 129, 157, 164, 173, 179  
 Cannizzo, 483  
 Cantone, 225, 254, 255, 445, 482  
 Carrière, 277, 411-17, 435-45  
 Caspari, 110  
 Cayla, 55  
 Chauveau, 455  
 Cheneveau, 256, 356-7  
  
 Claperyon, 501  
 Clingett, 32  
 Cockerill, 135  
 Cohen, 78, 79  
 Contino, 254, 255, 445  
 Coolidge, 311  
 Corbino, 478, 483  
 Corporaal, 20  
 Cramer, 10  
 Cranor, 366  
  
 Davies, 311  
 Day, 3, 309, 311-13, 314, 363  
 Dearle, 477  
 Dekker, 35, 63, 64, 77, 80, 93, 113, 118  
 Denier, 50  
 Dietzel, 424  
 Ditmar, 37, 110, 367, 389, 391  
 Douty, 446  
 Dubosc, 25, 303  
  
 Eaton, 46, 50-3, 57, 75, 105, 123, 131, 134, 141, 144, 146, 148-9, 152, 157, 158, 161-2, 164, 170, 177, 178-83, 186-9, 191, 203, 205, 290, 291, 295, 301, 309, 311-13, 314, 317, 321, 333-5, 337-9, 344, 346-7, 356, 359-60, 363, 375, 382, 396-401, 449  
 Ercolini, 478, 481, 483  
 Erdmann, 308  
 Esch, 92, 122, 148  
 Exner, 461-3  
  
 Faraday, 58, 108  
 Fessenden, 257-8, 460  
 Fickendy, 44, 101, 105  
 Fitting, 21  
 Flint, 66  
 Flower, 311, 315, 338, 359, 361, 388, 395-6  
 Fol, 59, 95, 313-14, 323, 324, 361, 388-9, 390, 404  
 Fonrobert, 304-5  
 Fourcroy, 57  
 Fox, 105  
 Frank, F., 118, 201, 403  
 Frank, O., 494

- Gallagher, 14  
 Galletly, 115  
 Gaunt, 311  
 Geer, 371  
 Girard, 65, 66  
 Gladstone, 108  
 Goldsbrough, 60, 208; 331-2, 351-6, 398, 403  
 Gordon, 479  
 Gorter, 4, 53, 63, 71, 72, 97, 101, 102, 137, 191, 403, 405  
 Gottlob, 196, 316, 381  
 Gough, 453  
 Govi, 459  
 Grädinger, 201  
 Graetz, 254, 464-5  
 Grantham, 6, 14, 29, 46, 50, 53, 94, 123, 131, 152, 157, 178, 186-9, 191, 195, 333-5, 350, 375, 396-401  
 Green, 108  
 Haberlandt, 23  
 Hamaker, 7, 11  
 Hancock, 286  
 Harries, 24, 42, 79, 115, 304-5  
 Hartjens, 137, 139, 140, 142  
 Hatschek, 33, 82, 353  
 Hausmaninger, 246-7  
 Hebb, 253-5  
 Heim, 256, 356-7  
 Hellendoorn, 133, 166-7, 177-8, 185, 325-33, 347, 353, 355, 449, 450-2  
 Henke, 72  
 Henri, 31, 32, 34, 36, 39, 44, 48, 102  
 Henriques, 310  
 Herbst, 96, 97, 98  
 Hesehus, 459  
 Heurn, van, 42, 89, 129, 154, 156, 163, 251-2, 283-5, 287, 291-2, 293, 296-7, 302, 313-14, 315, 323, 324, 361, 388-9, 390, 392, 393, 403, 404  
 Hibbert, 108  
 Hillen, 78, 79  
 Hinrichsen, 42, 76, 77, 78, 80  
 Hofmann, 25, 95, 196  
 Howie, 114  
 Ingersol, 219, 417  
 Iterson, van, 90, 139, 198, 297-8, 308, 337  
 Jong, de, 19, 20, 21, 41, 43, 44, 66, 76  
 Joule, 453-4, 456-7, 490  
 Julius, 479-80  
 Kemp, 454-5, 470  
 Kerbosch, 70, 98, 137, 140  
 Keuchenius, 12, 27  
 Kindscher, 42  
 Kirchhof, 97, 98, 101, 107, 307, 404  
 Knapp, 6, 29  
 Kniep, 23, 24, 26  
 Kohlrausch, 426-33, 435, 437  
 Koketsu, 24, 56  
 Korteweg, 479-80  
 Kratz, 93, 113, 114, 115, 311, 315, 338, 359, 361, 388, 395-6, 409  
 Krayenhoff, van der Leur, 164  
 Kundt, 476  
 Kurz, 244  
 Lampa, 483  
 Lebedeff, 471  
 Leon, 96  
 Lewis, 104  
 Lock, 11, 19, 28  
 Lundal, 455-6, 458, 466, 471, 489-90, 502  
 Luttringer, 25  
 Maas, 29, 30, 137  
 Mallock, 211, 226-7, 230, 234, 252-3, 255-6, 259, 277, 501  
 Maquenne, 66, 68  
 Marcusson, 76, 77, 78, 80  
 Martin, 148  
 Memmler, 248, 260, 262, 265, 266, 267, 270, 272-6, 278-9, 339  
 Miller, 95  
 Mohr, 14  
 Molisch, 24, 28  
 Morgan, 105, 145, 152  
 Müller, 78  
 Naccari, 494  
 Neesen, 424-6  
 Ono, 358  
 Ostromislenski, 286, 307  
 Ostwald, 97, 304, 306  
 Page, 453  
 Parkin, 144  
 Payen, 41  
 Peachey, 96, 97  
 Fetch, 12  
 Phillips, 434-5, 437, 445  
 Pickles, 67  
 Potts, 309, 311  
 Pratt, 477  
 Pulfrich, 433-4, 476-7, 494-5  
 Racibowski, 54  
 Reinhardt, 311  
 Romburgh, van, 4, 79  
 Röntgen, 490-3  
 Rosenstein, 311

- Rossem, van, 84, 105, 107, 122, 198  
     199, 204-5, 267, 296-7, 341,  
     362, 381, 404-5, 420-1, 449  
 Rossi, 475-6  
 Rothe, 310  
 Rubens, 477  
 Russner, 463-4, 465, 471, 472, 473  
 Rutgers, 5, 7, 13, 21, 137  
  
 Sack, 78  
 Schidrowitz, 39, 45, 60, 208, 291,  
     331-2, 350-6, 398, 402, 403,  
     404, 423, 446, 448  
 Schiller, L., 255, 483, 493, 494, 496-7  
 Schiller, N., 478  
 Schippel, 489, 498-500  
 Schmitz, 112, 114  
 Schmulewitsch, 358, 460-1  
 Schneebeli, 244-5  
 Schob, 260, 262, 265, 266, 267, 270,  
     272-6, 278-9  
 Schwartz, 270, 413, 416, 417-19, 445,  
     446-7, 454-5, 470  
 Scott, 81, 197  
 Seidl, 393  
 Sharples, 4, 27, 160, 161  
 Shedd, 219, 417  
 Sievers, 41  
 Simon, 21  
 Skellon, 307, 314, 325  
 Skinner, 12, 13  
 Spence, 25, 26, 40, 43, 50, 54, 55,  
     56, 66, 72, 79, 81, 83, 91, 93,  
     101, 109, 113, 114, 115, 121,  
     196, 292-3, 303-4, 306, 307,  
     313, 323, 358, 371-4, 409  
 Spiller, 95  
 Spoon, 205-8, 214-15, 216, 299-300  
 Sprecher, 11  
 Spring, 3, 15  
 Stefan, 461  
 Stévant, 220, 211, 226, 250-1, 259-  
     60, 270  
 Stevens, 31, 32, 37, 38-9, 40, 42,  
     45, 48, 61-2, 72, 80, 84, 85-8,  
     91-2, 111-12, 119, 120-2, 152,  
     189-90, 248-9, 275, 277, 286,  
     305, 314, 348, 358, 363-5,  
     368-71, 381, 390, 391-2, 394-5,  
     396, 403, 413, 419-20, 448  
 Swart, 53  
  
 Thieben, 389, 391  
 Thomas, 459, 471, 489  
 Thomson, 104  
 Thomson, 454  
 Tollens, 66, 77  
 Tromp de Haas, 9, 41, 43, 44  
 Tschirch, 41, 43, 78, 112, 113  
 Tuttle, 310  
 Twiss, 33, 52, 305, 308  
  
 Ulltée, 128, 137, 145, 152, 165, 215,  
     408, 409  
  
 Vernet, 24, 37, 44, 45, 46, 50, 51,  
     137  
 Villari, 221, 225-6, 234, 259, 410,  
     471, 488, 489  
 Vries, de, 43, 64, 75, 81, 129, 130,  
     132-3, 136, 137, 141, 146, 148,  
     149, 153-4, 157, 166-7, 177-8,  
     183, 184-5, 193-5, 205-8, 216,  
     299-300, 319-21, 324, 325-33,  
     347, 350, 351, 352, 355, 356,  
     362, 363, 375-80, 405-9, 449,  
     450-2  
  
 Walker, 97, 105, 107, 199, 359  
 Ward, 83, 91, 292-3  
 Warming, 26  
 Waters, 310  
 Weber, C. O., 33, 40, 41, 43, 54,  
     66, 77, 95, 108, 292, 303, 306,  
     313  
 Weber, L. E., 77, 90  
 Went, 23  
 Wertheim, 487-8, 493  
 Whitby, 5-7, 10, 13, 25, 31, 38, 45,  
     46-7, 49-57, 60, 96-7, 101,  
     102-4, 107, 131, 138, 163, 173,  
     174, 179, 181, 188, 199, 202-3,  
     209, 213, 290, 350, 359  
 Whitfield, 67  
 Wiegand, 39, 484, 500  
 Williams, 154  
 Wormeley, 279-80  
 Wright, C. H., 14  
 Wright, H., 14  
  
 Young, 83, 121, 313, 323, 374  
  
 Zilchert, 82